

are not available. The instrument relative error shall be  $\leq 10$  percent of the certified value of the audit gas.

#### 8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Installation and Measurement Location Specifications. Install the CEMs in a location where the measurements are representative of the source emissions. Consider other factors, such as ease of access for calibration and maintenance purposes. The location should not be close to air in-leakages. The sampling location should be at least two equivalent duct diameters downstream from the nearest control device, point of pollutant generation, or other point at which a change in the pollutant concentration or emission rate occurs. The location should be at least 0.5 diameter upstream from the exhaust or control device. To calculate equivalent duct diameter, see Section 12.2 of Method 1 (40 CFR Part 60, Appendix A). Sampling locations not conforming to the requirements in this section may be used if necessary upon approval of the Administrator.

8.2 Pretest Preparation Period. Using the procedures described in Method 18 (40 CFR Part 60, Appendix A), perform initial tests to determine GC conditions that provide good resolution and minimum analysis time for compounds of interest. Resolution interferences that may occur can be eliminated by appropriate GC column and detector choice or by shifting the retention times through changes in the column flow rate and the use of temperature programming.

8.3 7-Day Calibration Error (CE) Test Period. At the beginning of each 24-hour period, set the initial instrument setpoints by conducting a multi-point calibration for each compound. The

multi-point calibration shall meet the requirements in Section 13.3. Throughout the 24-hour period, sample and analyze the stack gas at the sampling intervals prescribed in the regulation or permit. At the end of the 24 hour period, inject the three calibration gases for each compound in triplicate and determine the average instrument response. Determine the CE for each pollutant at each level using the equation in Section 9-2.

Each CE shall be  $\leq 10$  percent. Repeat this procedure six more times for a total of 7 consecutive days.

8.4 Performance Audit Test Periods. Conduct the performance audit once during the initial 7-day CE test and quarterly thereafter. Sample and analyze the EPA audit gas(es) (or the gas mixture prepared by EPA's traceability protocol if an EPA audit gas is not available) three times. Calculate the average instrument response. Report the audit results as part of the reporting requirements in the appropriate regulation or permit (if using a gas mixture, report the certified cylinder concentration of each pollutant).

8.5 Reporting. Follow the reporting requirements of the applicable regulation or permit. If the reporting requirements include the results of this performance specification, summarize in tabular form the results of the CE tests. Include all data sheets, calculations, CEMS data records, performance audit results, and calibration gas concentrations and certifications.

#### 9.0 Quality Control [Reserved]

#### 10.0 Calibration and Standardization

10.1 Initial Multi-Point Calibration. After initial startup of the GC, after routine maintenance or repair, or at least once per month, conduct a multi-

point calibration of the GC for each target analyte. The multi-point calibration for each analyte shall meet the requirements in Section 13.3.

10.2 Daily Calibration. Once every 24 hours, analyze the mid-level calibration standard for each analyte in triplicate. Calculate the average instrument response for each analyte. The average instrument response shall not vary more than 10 percent from the certified concentration value of the cylinder for each analyte. If the difference between the analyzer response and the cylinder concentration for any target compound is greater than 10 percent, immediately inspect the instrument making any necessary adjustments, and conduct an initial multi-point calibration as described in Section 10.1.

#### 11.0 Analytical Procedure. Sample Collection and Analysis Are Concurrent for This Performance Specification (See Section 8.0)

#### 12.0 Calculations and Data Analysis

##### 12.1 Nomenclature.

$C_m$  = average instrument response, ppm.

$C_a$  = cylinder gas value, ppm.

$F$  = Flow rate of stack gas through sampling system, in Liters/min.

$n$  = Number of measurement points.

$r^2$  = Coefficient of determination.

$V$  = Sample system volume, in Liters, which is the volume inside the sample probe and tubing leading from the stack to the sampling loop.

$x$  = CEMS response.

$y$  = Actual value of calibration standard.

##### 12.2 Coefficient of Determination.

Calculate  $r^2$  using linear regression analysis and the average concentrations obtained at three calibration points as shown in Equation 9-1.

$$r^2 = \left( \frac{n \sum x_i y_i - (\sum x_i)(\sum y_i)}{\sqrt{(n \sum y_i^2 - \sum y_i \sum y_i)(n \sum x_i^2 - \sum x_i \sum x_i)}} \right)^2 \quad \text{Eq. 9-1}$$

12.3 Calibration Error Determination. Determine the percent calibration error (CE) at each concentration for each pollutant using the following equation.

$$CE = \frac{C_m - C_a}{C_a} \times 100 \quad \text{Eq. 9-2}$$

#### 12.4 Sampling System Time Constant (T).

$$T = \frac{F}{V} \quad \text{Eq. 9-3}$$

#### 13.0 Method Performance

13.1 Calibration Error (CE). The CEMS must allow the determination of CE at all three calibration levels. The average CEMS calibration response must not differ by more than 10 percent of calibration gas value at each level after each 24-hour period of the initial test.

13.2 Calibration Precision and Linearity. For each triplicate injection at each concentration level for each target

analyte, any one injection shall not deviate more than 5 percent from the average concentration measured at that level. The linear regression curve for each organic compound at all three levels shall have an  $r^2 \geq 0.995$  (using Equation 9-1).

13.3 Measurement Frequency. The sample to be analyzed shall flow continuously through the sampling system. The sampling system time

constant shall be  $\leq 5$  minutes or the sampling frequency specified in the applicable regulation, whichever is less. Use Equation 9-3 to determine T. The analytical system shall be capable of measuring the effluent stream at the frequency specified in the appropriate regulation or permit.

14.0 *Pollution Prevention.* [Reserved]

15.0 *Waste Management.* [Reserved]

16.0 *References.* [Reserved]

17.0 *Tables, Diagrams, Flowcharts, and Validation Data* [Reserved]

218. In Part 60, Appendix B is amended by adding Performance Specification 15 as follows:

#### **Appendix B—Performance Specifications**

\* \* \* \* \*

#### **Performance Specification 15— Performance Specification for Extractive FTIR Continuous Emissions Monitor Systems in Stationary Sources**

##### *1.0 Scope and Application*

1.1 *Analytes.* This performance specification is applicable for measuring all hazardous air pollutants (HAPs) which absorb in the infrared region and can be quantified using Fourier Transform Infrared Spectroscopy (FTIR), as long as the performance criteria of this performance specification are met. This specification is to be used for evaluating FTIR continuous emission monitoring systems for measuring HAPs regulated under Title III of the 1990 Clean Air Act Amendments. This specification also applies to the use of FTIR CEMs for measuring other volatile organic or inorganic species.

1.2 *Applicability.* A source which can demonstrate that the extractive FTIR system meets the criteria of this performance specification for each regulated pollutant may use the FTIR system to continuously monitor for the regulated pollutants.

##### *2.0 Summary of Performance Specification*

For compound-specific sampling requirements refer to FTIR sampling methods (e.g., reference 1). For data reduction procedures and requirements refer to the EPA FTIR Protocol (reference 2), hereafter referred to as the "FTIR Protocol." This specification describes sampling and analytical procedures for quality assurance. The infrared spectrum of any absorbing compound provides a distinct signature. The infrared spectrum of a mixture contains the superimposed spectra of each mixture component. Thus, an FTIR

CEM provides the capability to continuously measure multiple components in a sample using a single analyzer. The number of compounds that can be speciated in a single spectrum depends, in practice, on the specific compounds present and the test conditions.

##### *3.0 Definitions*

For a list of definitions related to FTIR spectroscopy refer to Appendix A of the FTIR Protocol. Unless otherwise specified, spectroscopic terms, symbols and equations in this performance specification are taken from the FTIR Protocol or from documents cited in the Protocol. Additional definitions are given below.

##### *3.1 FTIR Continuous Emission Monitoring System (FTIR CEM).*

3.1.1 *FTIR System.* Instrument to measure spectra in the mid-infrared spectral region ( $500$  to  $4000\text{ cm}^{-1}$ ). It contains an infrared source, interferometer, sample gas containment cell, infrared detector, and computer. The interferometer consists of a beam splitter that divides the beam into two paths, one path a fixed distance and the other a variable distance. The computer is equipped with software to run the interferometer and store the raw digitized signal from the detector (interferogram). The software performs the mathematical conversion (the Fourier transform) of the interferogram into a spectrum showing the frequency dependent sample absorbance. All spectral data can be stored on computer media.

3.1.2 *Gas Cell.* A gas containment cell that can be evacuated. It contains the sample as the infrared beam passes from the interferometer, through the sample, and to the detector. The gas cell may have multi-pass mirrors depending on the required detection limit(s) for the application.

3.1.3 *Sampling System.* Equipment used to extract sample from the test location and transport the gas to the FTIR analyzer. Sampling system components include probe, heated line, heated non-reactive pump, gas distribution manifold and valves, flow measurement devices and any sample conditioning systems.

3.2 *Reference CEM.* An FTIR CEM, with sampling system, that can be used for comparison measurements.

3.3 *Infrared Band (also Absorbance Band or Band).* Collection of lines arising from rotational transitions superimposed on a vibrational transition. An infrared absorbance band is analyzed to determine the analyte concentration.

3.4 *Sample Analysis.* Interpreting infrared band shapes, frequencies, and intensities to obtain sample component concentrations. This is usually performed by a software routine using a classical least squares (cls), partial least squares (pls), or K- or P- matrix method.

3.5 *(Target) Analyte.* A compound whose measurement is required, usually to some established limit of detection and analytical uncertainty.

3.6 *Interferant.* A compound in the sample matrix whose infrared spectrum overlaps at least part of an analyte spectrum complicating the analyte measurement. The interferant may not prevent the analyte measurement, but could increase the analytical uncertainty in the measured concentration. Reference spectra of interferants are used to distinguish the interferant bands from the analyte bands. An interferant for one analyte may not be an interferant for other analytes.

3.7 *Reference Spectrum.* Infrared spectra of an analyte, or interferant, prepared under controlled, documented, and reproducible laboratory conditions (see Section 4.6 of the FTIR Protocol). A suitable library of reference spectra can be used to measure target analytes in gas samples.

3.8 *Calibration Spectrum.* Infrared spectrum of a compound suitable for characterizing the FTIR instrument configuration (Section 4.5 in the FTIR Protocol).

3.9 *One hundred percent line.* A double beam transmittance spectrum obtained by combining two successive background single beam spectra. Ideally, this line is equal to 100 percent transmittance (or zero absorbance) at every point in the spectrum. The zero absorbance line is used to measure the RMS noise of the system.

3.10 *Background Deviation.* Any deviation (from 100 percent) in the one hundred percent line (or from zero absorbance). Deviations greater than  $\pm 5$  percent in any analytical region are unacceptable. Such deviations indicate a change in the instrument throughput relative to the single-beam background.

3.11 *Batch Sampling.* A gas cell is alternately filled and evacuated. A Spectrum of each filled cell (one discrete sample) is collected and saved.

3.12 *Continuous Sampling.* Sample is continuously flowing through a gas cell. Spectra of the flowing sample are collected at regular intervals.

3.13 *Continuous Operation.* In continuous operation an FTIR CEM system, without user intervention, samples flue gas, records spectra of samples, saves the spectra to a disk, analyzes the spectra for the target

analytes, and prints concentrations of target analytes to a computer file. User intervention is permitted for initial set-up of sampling system, initial calibrations, and periodic maintenance.

**3.14 Sampling Time.** In batch sampling—the time required to fill the cell with flue gas. In continuous sampling—the time required to collect the infrared spectrum of the sample gas.

**3.15 PPM-Meters.** Sample concentration expressed as the concentration-path length product, ppm (molar) concentration multiplied by the path length of the FTIR gas cell. Expressing concentration in these units provides a way to directly compare measurements made using systems with different optical configurations. Another useful expression is (ppm-meters)/K, where K is the absolute temperature of the sample in the gas cell.

**3.16 CEM Measurement Time Constant.** The Time Constant (TC, minutes for one cell volume to flow through the cell) determines the minimum interval for complete removal of an analyte from the FTIR cell. It depends on the sampling rate ( $R_s$  in Lpm), the FTIR cell volume ( $V_{cell}$  in L) and the chemical and physical properties of an analyte.

$$TC = \frac{V_{cell}}{R_s} \quad \text{Eq. 1}$$

For example, if the sample flow rate (through the FTIR cell) is 5 Lpm and the cell volume is 7 liters, then TC is equal to 1.4 minutes (0.71 cell volumes per minute). This performance specification defines  $5 * TC$  as the minimum interval between independent samples.

**3.17 Independent Measurement.** Two independent measurements are spectra of two independent samples. Two independent samples are separated by, at least 5 cell volumes. The interval between independent measurements depends on the cell volume and the sample flow rate (through the cell). There is no mixing of gas between two independent samples. Alternatively, estimate the analyte residence time empirically: (1) Fill cell to ambient pressure with a (known analyte concentration) gas standard, (2) measure the spectrum of the gas standard, (3) purge the cell with zero gas at the sampling rate and collect a spectrum every minute until the analyte standard is no longer detected spectroscopically. If the measured time corresponds to less than 5 cell volumes, use  $5 * TC$  as the minimum interval between independent measurements. If the measured time is greater than  $5 * TC$ , then use this time as the minimum interval between independent measurements.

**3.18 Test Condition.** A period of sampling where all process, and sampling conditions, and emissions remain constant and during which a single sampling technique and a single analytical program are used. One Run may include results for more than one test condition. Constant emissions means that the composition of the emissions remains approximately stable so that a single analytical program is suitable for analyzing all of the sample spectra. A greater than two-fold change in analyte or interferant concentrations or the appearance of additional compounds in the emissions, may constitute a new test condition and may require modification of the analytical program.

**3.19 Run.** A single Run consists of spectra (one spectrum each) of at least 10 independent samples over a minimum of one hour. The concentration results from the spectra can be averaged together to give a run average for each analyte measured in the test run.

#### 4.0 Interferences

Several compounds, including water, carbon monoxide, and carbon dioxide, are known interferences in the infrared region in which the FTIR instrument operates. Follow the procedures in the FTIR protocol for subtracting or otherwise dealing with these and other interferences.

#### 5.0 Safety

The procedures required under this performance specification may involve hazardous materials, operations, and equipment. This performance specification may not address all of the safety problems associated with these procedures. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicable regulatory limitations prior to performing these procedures. The CEMS users manual and materials recommended by this performance specification should be consulted for specific precautions to be taken.

#### 6.0 Equipment and Supplies

**6.1 Installation of sampling equipment** should follow requirements of FTIR test Methods such as references 1 and 3 and the EPA FTIR Protocol (reference 2). Select test points where the gas stream composition is representative of the process emissions. If comparing to a reference method, the probe tips for the FTIR CEM and the RM should be positioned close together using the same sample port if possible.

**6.2 FTIR Specifications.** The FTIR CEM must be equipped with reference

spectra bracketing the range of path length-concentrations (absorbance intensities) to be measured for each analyte. The effective concentration range of the analyzer can be adjusted by changing the path length of the gas cell or by diluting the sample. The optical configuration of the FTIR system must be such that maximum absorbance of any target analyte is no greater than 1.0 and the minimum absorbance of any target analyte is at least 10 times the RMSD noise in the analytical region. For example, if the measured RMSD in an analytical region is equal to  $10^{-3}$ , then the peak analyte absorbance is required to be at least 0.01. Adequate measurement of all of the target analytes may require changing path lengths during a run, conducting separate runs for different analytes, diluting the sample, or using more than one gas cell.

**6.3 Data Storage Requirements.** The system must have sufficient capacity to store all data collected in one week of routine sampling. Data must be stored to a write-protected medium, such as write-once-read-many (WORM) optical storage medium or to a password protected remote storage location. A back-up copy of all data can be temporarily saved to the computer hard drive. The following items must be stored during testing.

- At least one sample interferogram per sampling Run or one interferogram per hour, whichever is greater. This assumes that no sampling or analytical conditions have changed during the run.
- All sample absorbance spectra (about 12 per hr, 288 per day).
- All background spectra and interferograms (variable, but about 5 per day).
- All CTS spectra and interferograms (at least 2 each 24 hour period).
- Documentation showing a record of resolution, path length, apodization, sampling time, sampling conditions, and test conditions for all sample, CTS, calibration, and background spectra.

Using a resolution of  $0.5 \text{ cm}^{-1}$ , with analytical range of  $3500 \text{ cm}^{-1}$ , assuming about 65 Kbytes per spectrum and 130 Kb per interferogram, the storage requirement is about 164 Mb for one week of continuous sampling. Lower spectral resolution requires less storage capacity. All of the above data must be stored for at least two weeks. After two weeks, storage requirements include: (1) all analytical results (calculated concentrations), (2) at least 1 sample spectrum with corresponding background and sample interferograms for each test condition, (3) CTS and calibration spectra with at least one interferogram for CTS and all interferograms for calibrations, (4) a

record of analytical input used to produce results, and (5) all other documentation. These data must be stored according to the requirements of the applicable regulation.

#### 7.0 Reagents and Standards [Reserved]

#### 8.0 Sample Collection, Preservation, Storage, and Transport [Reserved]

#### 9.0 Quality Control

These procedures shall be used for periodic quarterly or semiannual QA/QC checks on the operation of the FTIR CEM. Some procedures test only the analytical program and are not intended as a test of the sampling system.

9.1 Audit Sample. This can serve as a check on both the sampling system and the analytical program.

9.1.1 Sample Requirements. The audit sample can be a mixture or a single component. It must contain target analyte(s) at approximately the expected flue gas concentration(s). If possible, each mixture component concentration should be NIST traceable ( $\pm 2$  percent accuracy). If a cylinder mixture standard(s) cannot be obtained, then, alternatively, a gas phase standard can be generated from a condensed phase analyte sample. Audit sample contents and concentrations are not revealed to the FTIR CEM operator until after successful completion of procedures in 5.3.2.

9.1.2 Test Procedure. An audit sample is obtained from the Administrator. Spike the audit sample using the analyte spike procedure in Section 11. The audit sample is measured directly by the FTIR system (undiluted) and then spiked into the effluent at a known dilution ratio. Measure a series of spiked and unspiked samples using the same procedures as those used to analyze the stack gas. Analyze the results using Sections 12.1 and 12.2. The measured concentration of each analyte must be within  $\pm 5$  percent of the expected concentration (plus the uncertainty), *i.e.*, the calculated correction factor must be within 0.93 and 1.07 for an audit with an analyte uncertainty of  $\pm 2$  percent.

9.2 Audit Spectra. Audit spectra can be used to test the analytical program of the FTIR CEM, but provide no test of the sampling system.

9.2.1 Definition and Requirements. Audit spectra are absorbance spectra that; (1) have been well characterized, and (2) contain absorbance bands of target analyte(s) and potential interferants at intensities equivalent to what is expected in the source effluent. Audit spectra are provided by the administrator without identifying information. Methods of preparing

Audit spectra include; (1) mathematically adding sample spectra or adding reference and interferant spectra, (2) obtaining sample spectra of mixtures prepared in the laboratory, or (3) they may be sample spectra collected previously at a similar source. In the last case it must be demonstrated that the analytical results are correct and reproducible. A record associated with each Audit spectrum documents its method of preparation. The documentation must be sufficient to enable an independent analyst to reproduce the Audit spectra.

9.2.2 Test Procedure. Audit spectra concentrations are measured using the FTIR CEM analytical program. Analytical results must be within  $\pm 5$  percent of the certified audit concentration for each analyte (plus the uncertainty in the audit concentration). If the condition is not met, demonstrate how the audit spectra are unrepresentative of the sample spectra. If the audit spectra are representative, modify the FTIR CEM analytical program until the test requirement is met. Use the new analytical program in subsequent FTIR CEM analyses of effluent samples.

9.3 Submit Spectra For Independent Analysis. This procedure tests only the analytical program and not the FTIR CEM sampling system. The analyst can submit FTIR CEM spectra for independent analysis by EPA. Requirements for submission include; (1) three representative absorbance spectra (and stored interferograms) for each test period to be reviewed, (2) corresponding CTS spectra, (3) corresponding background spectra and interferograms, (4) spectra of associated spiked samples if applicable, and (5) analytical results for these sample spectra. The analyst will also submit documentation of process times and conditions, sampling conditions associated with each spectrum, file names and sampling times, method of analysis and reference spectra used, optical configuration of FTIR CEM including cell path length and temperature, spectral resolution and apodization used for every spectrum. Independent analysis can also be performed on site in conjunction with the FTIR CEM sampling and analysis. Sample spectra are stored on the independent analytical system as they are collected by the FTIR CEM system. The FTIR CEM and the independent analyses are then performed separately. The two analyses will agree to within  $\pm 120$  percent for each analyte using the procedure in Section 12.3. This assumes both analytical routines have properly accounted for differences in optical path

length, resolution, and temperature between the sample spectra and the reference spectra.

#### 10.0 Calibration and Standardization

10.1 Calibration Transfer Standards. For CTS requirements see Section 4.5 of the FTIR Protocol. A well characterized absorbance band in the CTS gas is used to measure the path length and line resolution of the instrument. The CTS measurements made at the beginning of every 24 hour period must agree to within  $\pm 5$  percent after correction for differences in pressure.

Verify that the frequency response of the instrument and CTS absorbance intensity are correct by comparing to other CTS spectra or by referring to the literature.

10.2 Analyte Calibration. If EPA library reference spectra are not available, use calibration standards to prepare reference spectra according to Section 6 of the FTIR Protocol. A suitable set of analyte reference data includes spectra of at least 2 independent samples at each of at least 2 different concentrations. The concentrations bracket a range that includes the expected analyte absorbance intensities. The linear fit of the reference analyte band areas must have a fractional calibration uncertainty (FCU in Appendix F of the FTIR Protocol) of no greater than 10 percent. For requirements of analyte standards refer to Section 4.6 of the FTIR Protocol.

10.3 System Calibration. The calibration standard is introduced at a point on the sampling probe. The sampling system is purged with the calibration standard to verify that the absorbance measured in this way is equal to the absorbance in the analyte calibration. Note that the system calibration gives no indication of the ability of the sampling system to transport the target analyte(s) under the test conditions.

10.4 Analyte Spike. The target analyte(s) is spiked at the outlet of the sampling probe, upstream of the particulate filter, and combined with effluent at a ratio of about 1 part spike to 9 parts effluent. The measured absorbance of the spike is compared to the expected absorbance of the spike plus the analyte concentration already in the effluent. This measures sampling system bias, if any, as distinguished from analyzer bias. It is important that spiked sample pass through all of the sampling system components before analysis.

10.5 Signal-to-Noise Ratio (S/N). The measure of S/N in this performance specification is the root-mean-square (RMS) noise level as given in Appendix

C of the FTIR Protocol. The RMS noise level of a contiguous segment of a spectrum is defined as the RMS difference (RMSD) between the  $n$  contiguous absorbance values ( $A_i$ ) which form the segment and the mean value ( $A_m$ ) of that segment.

$$\text{RMSD} = \sqrt{\left(\frac{1}{n}\right) \sum_{i=1}^n (A_i - A_m)^2} \quad \text{Eq. 2}$$

A decrease in the S/N may indicate a loss in optical throughput, or detector or interferometer malfunction.

**10.6 Background Deviation.** The 100 percent baseline must be between 95 and 105 percent transmittance (absorbance of 0.02 to  $-0.02$ ) in every analytical region. When background deviation exceeds this range, a new background spectrum must be collected using nitrogen or other zero gas.

**10.7 Detector Linearity.** Measure the background and CTS at three instrument aperture settings; one at the aperture setting to be used in the testing, and one each at settings one half and twice the test aperture setting. Compare the three CTS spectra. CTS band areas should agree to within the uncertainty of the cylinder standard. If test aperture is the maximum aperture, collect CTS spectrum at maximum aperture, then close the aperture to reduce the IR throughput by half. Collect a second background and CTS at the smaller aperture setting and compare the spectra as above. Instead of changing the aperture neutral density filters can be used to attenuate the infrared beam. Set up the FTIR system as it will be used in the test measurements. Collect a CTS spectrum. Use a neutral density filter to attenuate the infrared beam (either immediately after the source or the interferometer) to approximately  $\frac{1}{2}$  its original intensity. Collect a second CTS spectrum. Use another filter to attenuate the infrared beam to approximately  $\frac{1}{4}$  its original intensity. Collect a third background and CTS spectrum. Compare the CTS spectra as above. Another check on linearity is to observe the single beam background in frequency regions where the optical configuration is known to have a zero response. Verify that the detector response is "flat" and equal to zero in these regions. If detector response is not linear, decrease aperture, or attenuate the infrared beam. Repeat the linearity check until system passes the requirement.

### 11.0 Analytical Procedure

**11.1 Initial Certification.** First, perform the evaluation procedures in Section 6.0 of the FTIR Protocol. The performance of an FTIR CEM can be

certified upon installation using EPA Method 301 type validation (40 CFR, Part 63, Appendix A), or by comparison to a reference Method if one exists for the target analyte(s). Details of each procedure are given below. Validation testing is used for initial certification upon installation of a new system. Subsequent performance checks can be performed with more limited analyte spiking. Performance of the analytical program is checked initially, and periodically as required by EPA, by analyzing audit spectra or audit gases.

**11.1.1 Validation.** Use EPA Method 301 type sampling (reference 4, Section 5.3 of Method 301) to validate the FTIR CEM for measuring the target analytes. The analyte spike procedure is as follows: (1) a known concentration of analyte is mixed with a known concentration of a non-reactive tracer gas, (2) the undiluted spike gas is sent directly to the FTIR cell and a spectrum of this sample is collected, (3) pre-heat the spiked gas to at least the sample line temperature, (4) introduce spike gas at the back of the sample probe upstream of the particulate filter, (5) spiked effluent is carried through all sampling components downstream of the probe, (6) spike at a ratio of roughly 1 part spike to 9 parts flue gas (or more dilute), (7) the spike-to-flue gas ratio is estimated by comparing the spike flow to the total sample flow, and (8) the spike ratio is verified by comparing the tracer concentration in spiked flue gas to the tracer concentration in undiluted spike gas. The analyte flue gas concentration is unimportant as long as the spiked component can be measured and the sample matrix (including interferences) is similar to its composition under test conditions. Validation can be performed using a single FTIR CEM analyzing sample spectra collected sequentially. Since flue gas analyte (unspiked) concentrations can vary, it is recommended that two separate sampling lines (and pumps) are used; one line to carry unspiked flue gas and the other line to carry spiked flue gas. Even with two sampling lines the variation in unspiked concentration may be fast compared to the interval between consecutive measurements. Alternatively, two FTIR CEMs can be operated side-by-side, one measuring spiked sample, the other unspiked sample. In this arrangement spiked and unspiked measurements can be synchronized to minimize the affect of temporal variation in the unspiked analyte concentration. In either sampling arrangement, the interval between measured concentrations used

in the statistical analysis should be, at least, 5 cell volumes ( $5 * TC$  in equation 1). A validation run consists of, at least, 24 independent analytical results, 12 spiked and 12 unspiked samples. See Section 3.17 for definition of an "independent" analytical result. The results are analyzed using Sections 12.1 and 12.2 to determine if the measurements passed the validation requirements. Several analytes can be spiked and measured in the same sampling run, but a separate statistical analysis is performed for each analyte. In lieu of 24 independent measurements, averaged results can be used in the statistical analysis. In this procedure, a series of consecutive spiked measurements are combined over a sampling period to give a single average result. The related unspiked measurements are averaged in the same way. The minimum 12 spiked and 12 unspiked result averages are obtained by averaging measurements over subsequent sampling periods of equal duration. The averaged results are grouped together and statistically analyzed using Section 12.2.

**11.1.1.1 Validation with a Single Analyzer and Sampling Line.** If one sampling line is used, connect the sampling system components and purge the entire sampling system and cell with at least 10 cell volumes of sample gas. Begin sampling by collecting spectra of 2 independent unspiked samples. Introduce the spike gas into the back of the probe, upstream of the particulate filter. Allow 10 cell volumes of spiked flue gas to purge the cell and sampling system. Collect spectra of 2 independent spiked samples. Turn off the spike flow and allow 10 cell volumes of unspiked flue gas to purge the FTIR cell and sampling system. Repeat this procedure 6 times until the 24 samples are collected. Spiked and unspiked samples can also be measured in groups of 4 instead of in pairs. Analyze the results using Sections 12.1 and 12.2. If the statistical analysis passes the validation criteria, then the validation is completed. If the results do not pass the validation, the cause may be that temporal variations in the analyte sample gas concentration are fast relative to the interval between measurements. The difficulty may be avoided by: (1) Averaging the measurements over long sampling periods and using the averaged results in the statistical analysis, (2) modifying the sampling system to reduce TC by, for example, using a smaller volume cell or increasing the sample flow rate, (3) using two sample lines (4) use two analyzers to perform synchronized

measurements. This performance specification permits modifications in the sampling system to minimize TC if the other requirements of the validation sampling procedure are met.

**11.1.1.1.2 Validation With a Single Analyzer and Two Sampling Lines.** An alternative sampling procedure uses two separate sample lines, one carrying spiked flue gas, the other carrying unspiked gas. A valve in the gas distribution manifold allows the operator to choose either sample. A short heated line connects the FTIR cell to the 3-way valve in the manifold. Both sampling lines are continuously purged. Each sample line has a rotameter and a bypass vent line after the rotameter, immediately upstream of the valve, so that the spike and unspiked sample flows can each be continuously monitored. Begin sampling by collecting spectra of 2 independent unspiked samples. Turn the sampling valve to close off the unspiked gas flow and allow the spiked flue gas to enter the FTIR cell. Isolate and evacuate the cell and fill with the spiked sample to ambient pressure. (While the evacuated cell is filling, prevent air leaks into the cell by making sure that the spike sample rotameter always indicates that a portion of the flow is directed out the by-pass vent.) Open the cell outlet valve to allow spiked sample to continuously flow through the cell. Measure spectra of 2 independent spiked samples. Repeat this procedure until at least 24 samples are collected.

**11.1.1.1.3 Synchronized Measurements With Two Analyzers.** Use two FTIR analyzers, each with its own cell, to perform synchronized spiked and unspiked measurements. If possible, use a similar optical configuration for both systems. The optical configurations are compared by measuring the same CTS gas with both analyzers. Each FTIR system uses its own sampling system including a separate sampling probe and sampling line. A common gas distribution manifold can be used if the samples are never mixed. One sampling system and analyzer measures spiked effluent. The other sampling system and analyzer measures unspiked flue gas. The two systems are synchronized so that each measures spectra at approximately the same times. The sample flow rates are also synchronized so that both sampling rates are approximately the same ( $TC_1 \sim TC_2$  in equation 1). Start both systems at the same time. Collect spectra of at least 12 independent samples with each (spiked and unspiked) system to obtain the minimum 24 measurements. Analyze the analytical results using Sections 12.1 and 12.2. Run averages

can be used in the statistical analysis instead of individual measurements.

**11.1.1.4 Compare to a Reference Method (RM).** Obtain EPA approval that the method qualifies as an RM for the analyte(s) and the source to be tested. Follow the published procedures for the RM in preparing and setting up equipment and sampling system, performing measurements, and reporting results. Since FTIR CEMS have multicomponent capability, it is possible to perform more than one RM simultaneously, one for each target analyte. Conduct at least 9 runs where the FTIR CEM and the RM are sampling simultaneously. Each Run is at least 30 minutes long and consists of spectra of at least 5 independent FTIR CEM samples and the corresponding RM measurements. If more than 9 runs are conducted, the analyst may eliminate up to 3 runs from the analysis if at least 9 runs are used.

**11.1.1.4.1 RMs Using Integrated Sampling.** Perform the RM and FTIR CEM sampling simultaneously. The FTIR CEM can measure spectra as frequently as the analyst chooses (and should obtain measurements as frequently as possible) provided that the measurements include spectra of at least 5 independent measurements every 30 minutes. Concentration results from all of the FTIR CEM spectra within a run may be averaged for use in the statistical comparison even if all of the measurements are not independent. When averaging the FTIR CEM concentrations within a run, it is permitted to exclude some measurements from the average provided the minimum of 5 independent measurements every 30 minutes are included: The Run average of the FTIR CEM measurements depends on both the sample flow rate and the measurement frequency (MF). The run average of the RM using the integrated sampling method depends primarily on its sampling rate. If the target analyte concentration fluctuates significantly, the contribution to the run average of a large fluctuation depends on the sampling rate and measurement frequency, and on the duration and magnitude of the fluctuation. It is, therefore, important to carefully select the sampling rate for both the FTIR CEM and the RM and the measurement frequency for the FTIR CEM. The minimum of 9 run averages can be compared according to the relative accuracy test procedure in Performance Specification 2 for SO<sub>2</sub> and NO<sub>x</sub> CEMS (40 CFR, Part 60, App. B).

**11.1.1.4.2 RMs Using a Grab Sampling Technique.** Synchronize the RM and FTIR CEM measurements as

closely as possible. For a grab sampling RM record the volume collected and the exact sampling period for each sample. Synchronize the FTIR CEM so that the FTIR measures a spectrum of a similar cell volume at the same time as the RM grab sample was collected. Measure at least 5 independent samples with both the FTIR CEM and the RM for each of the minimum 9 Runs. Compare the Run concentration averages by using the relative accuracy analysis procedure in 40 CFR, Part 60, App. B.

**11.1.1.4.3 Continuous Emission Monitors (CEMs) as RMs.** If the RM is a CEM, synchronize the sampling flow rates of the RM and the FTIR CEM. Each run is at least 1-hour long and consists of at least 10 FTIR CEM measurements and the corresponding 10 RM measurements (or averages). For the statistical comparison use the relative accuracy analysis procedure in 40 CFR, Part 60, App. B. If the RM time constant is  $< \frac{1}{2}$  the FTIR CEM time constant, brief fluctuations in analyte concentrations which are not adequately measured with the slower FTIR CEM time constant can be excluded from the run average along with the corresponding RM measurements. However, the FTIR CEM run average must still include at least 10 measurements over a 1-hr period.

## 12.0 Calculations and Data Analysis

**12.1 Spike Dilution Ratio, Expected Concentration.** The Method 301 bias is calculated as follows.

$$B = S_m - M_m - CS \quad \text{Eq. 3}$$

Where:

B = Bias at the spike level

$S_m$  = Mean of the observed spiked sample concentrations

$M_m$  = Mean of the observed unspiked sample concentrations

CS = Expected value of the spiked concentration.

The CS is determined by comparing the SF<sub>6</sub> tracer concentration in undiluted spike gas to the SF<sub>6</sub> tracer concentrations in the spiked samples;

$$DF = \frac{[SF_6]_{\text{direct}}}{[SF_6]_{\text{spiked}}} \quad \text{Eq. 4}$$

The expected concentration (CS) is the measured concentration of the analyte in undiluted spike gas divided by the dilution factor

$$CS = \frac{[anal]_{\text{dir}}}{DF} \quad \text{Eq. 5}$$

Where:

$[anal]_{dir}$  = The analyte concentration in undiluted spike gas measured directly by filling the FTIR cell with the spike gas.

If the bias is statistically significant (Section 12.2), Method 301 requires that a correction factor, CF, be multiplied by

the analytical results, and that  $0.7 \leq CF \leq 1.3$ .

$$CF = \frac{1}{1 + \frac{B}{CS}} \quad \text{Eq. 6}$$

12.2 Statistical Analysis of Validation Measurements. Arrange the independent measurements (or measurement averages) as in Table 1. More than 12 pairs of measurements can be analyzed. The statistical analysis follows EPA Method 301, Section 6.3. Section 12.1 of this performance

specification shows the calculations for the bias, expected spike concentration, and correction factor. This Section shows the determination of the statistical significance of the bias. Determine the statistical significance of the bias at the 95 percent confidence level by calculating the t-value for the

set of measurements. First, calculate the differences,  $d_i$ , for each pair of spiked and each pair of unspiked measurements. Then calculate the standard deviation of the spiked pairs of measurements.

$$SD_s = \sqrt{\frac{\sum d_i^2}{2n}} \quad \text{Eq. 7}$$

Where:

$d_i$  = The differences between pairs of spiked measurements.

$SD_s$  = The standard deviation in the  $d_i$  values.  
 $n$  = The number of spiked pairs,  $2n=12$  for the minimum of 12 spiked and 12 unspiked measurements.

Calculate the relative standard deviation, RSD, using  $SD_s$  and the mean of the spiked concentrations,  $S_m$ . The RSD must be  $\leq 50\%$ .

$$RSD = \left( \frac{SD}{S_m} \right) \quad \text{Eq. 8}$$

Repeat the calculations in equations 7 and 8 to determine  $SD_u$  and RSD,

respectively, for the unspiked samples. Calculate the standard deviation of the

mean using  $SD_s$  and  $SD_u$  from equation 7.

$$SD = \sqrt{SD_s^2 + SD_u^2} \quad \text{Eq. 9}$$

The t-statistic is calculated as follows to test the bias for statistical significance;

$$t = \frac{|B|}{SDM} \quad \text{Eq. 10}$$

where the bias, B, and the correction factor, CF, are given in Section 12.1. For 11 degrees of freedom, and a one-tailed distribution, Method 301 requires that  $t \leq 2.01$ . If the t-statistic indicates the bias is statistically significant, then analytical measurements must be multiplied by the correction factor.

There is no limitation on the number of measurements, but there must be at least 12 independent spiked and 12 independent unspiked measurements. Refer to the t-distribution (Table 2) at the 95 percent confidence level and appropriate degrees of freedom for the critical t-value.

## 16.0 References

1. Method 318, 40 CFR, Part 63, Appendix A (Draft), "Measurement of Gaseous Formaldehyde, Phenol and Methanol Emissions by FTIR Spectroscopy," EPA Contract No. 68D20163, Work Assignment 2-18, February, 1995.

2. "EPA Protocol for the Use of Extractive Fourier Transform Infrared (FTIR) Spectrometry in Analyses of Gaseous Emissions from Stationary Industrial Sources," February, 1995.

3. "Measurement of Gaseous Organic and Inorganic Emissions by Extractive FTIR Spectroscopy," EPA Contract No. 68-D2-0165, Work Assignment 3-08.

4. "Method 301—Field Validation of Pollutant Measurement Methods from Various Waste Media," 40 CFR 63, App A.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 1.—ARRANGEMENT OF VALIDATION MEASUREMENTS FOR STATISTICAL ANALYSIS

Measurement (or average)	Time	Spiked (ppm)	d <sub>i</sub> spiked	Unspiked (ppm)	d <sub>i</sub> unspiked
1 .....		S <sub>1</sub>	S <sub>2</sub> - S <sub>1</sub>	U <sub>1</sub>	U <sub>2</sub> - U <sub>1</sub>
2 .....		S <sub>2</sub>		U <sub>2</sub>	
3 .....		S <sub>3</sub>	S <sub>4</sub> - S <sub>3</sub>	U <sub>3</sub>	U <sub>4</sub> - U <sub>3</sub>
4 .....		S <sub>4</sub>		U <sub>4</sub>	
5 .....		S <sub>5</sub>	S <sub>6</sub> - S <sub>5</sub>	U <sub>5</sub>	U <sub>6</sub> - U <sub>5</sub>
6 .....		S <sub>6</sub>		U <sub>6</sub>	
7 .....		S <sub>7</sub>	S <sub>8</sub> - S <sub>7</sub>	U <sub>7</sub>	U <sub>8</sub> - U <sub>7</sub>
8 .....		S <sub>8</sub>		U <sub>8</sub>	
9 .....		S <sub>9</sub>	S <sub>10</sub> - S <sub>9</sub>	U <sub>9</sub>	U <sub>10</sub> - U <sub>9</sub>
10 .....		S <sub>10</sub>		U <sub>10</sub>	
11 .....		S <sub>11</sub>	S <sub>12</sub> - S <sub>11</sub>	U <sub>11</sub>	U <sub>12</sub> - U <sub>11</sub>
12 .....		S <sub>12</sub>		U <sub>12</sub>	
Average -> .....		S <sub>m</sub>		M <sub>m</sub>	

TABLE 2.—T=VALUES

n - 1 <sup>a</sup>	t - value	n - 1 <sup>a</sup>	t - value	n - 1 <sup>a</sup>	t - value	n - 1 <sup>a</sup>	t - value
11	2.201	17	2.110	23	2.069	29	2.045
12	2.179	18	2.101	24	2.064	30	2.042
13	2.160	19	2.093	25	2.060	40	2.021
14	2.145	20	2.086	26	2.056	60	2.000
15	2.131	21	2.080	27	2.052	120	1.980
16	2.120	22	2.074	28	2.048	8	1.960

(<sup>a</sup>)n is the number of independent pairs of measurements (a pair consists of one spiked and its corresponding unspiked measurement). Either discreet (independent) measurements in a single run, or run averages can be used.

\* \* \* \* \*

## PART 61—NATIONAL EMISSION STANDARDS FOR HAZARDOUS AIR POLLUTANTS

1. The authority citation for Part 61 continues to read as follows: 42 U.S.C. 7401, 7412, 7413, 7414, 7416, 7601, and 7602.

2. In § 61.18, paragraph (a) is revised to read as follows:

### § 61.18 Incorporation by reference.

\* \* \* \* \*

(a) The following materials are available for purchase from at least one of the following addresses: American Society for Testing and Materials (ASTM), 1916 Race Street, Philadelphia, PA 19103; or University Microfilms

International, 300 North Zeeb Road, Ann Arbor, MI 48106.

(1) ASTM D737-75, Standard Test Method for Air Permeability of Textile Fabrics, incorporation by reference (IBR) approved January 27, 1983 for § 61.23(a).

(2) ASTM D835-85, Standard Specification for Refined Benzene-485, IBR approved September 14, 1989 for § 61.270(a).

(3) ASTM D836-84, Standard Specification for Industrial Grade Benzene, IBR approved September 14, 1989 for § 61.270(a).

(4) ASTM D1193-77, 91, Standard Specification for Reagent Water, IBR approved for Appendix B: Method 101, Section 7.1.1; Method 101A, Section 7.1.1; and Method 104, Section 7.1; Method 108, Section 7.1.3; Method

108A, Section 7.1.1; Method 108B, Section 7.1.1; Method 108C, Section 7.1.1; and Method 111, Section 7.3.

(5) ASTM D2267-68, 78, 88, Aromatics in Light Naphthas and Aviation Gasoline by Gas Chromatography, IBR approved September 30, 1986, for § 61.67(h)(1).

(6) ASTM D2359-85a, 93, Standard Specification for Refined Benzene-535, IBR approved September 14, 1989 for § 61.270(a).

(7) ASTM D2382-76, 88, Heat of Combustion of Hydrocarbon Fuels by Bomb Calorimeter (High-Precision Method), IBR approved June 6, 1984 for § 61.245(e)(3).

(8) ASTM D2504-67, 77, 88, 93, Noncondensable Gases in C<sub>3</sub> and Lighter Hydrocarbon Products by Gas

Chromatography, IBR approved June 6, 1984 for § 61.245(e)(3).

(9) ASTM D2986-71, 78, 95a, Standard Method for Evaluation of Air, Assay Media by the Monodisperse DOP (Diocetyl Phthalate) Smoke Test, IBR approved for Appendix B: Method 103, Section 6.1.3.

(10) ASTM D4420-94, Standard Test Method for Determination of Aromatics in Finished Gasoline by Gas Chromatography, IBR approved for § 61.67(h)(1).

(11) ASTM D4734-87, 96, Standard Specification for Refined Benzene-545, IBR approved September 14, 1989 for § 61.270(a).

(12) ASTM D4809-95, Standard Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter (Precision Method), IBR approved for § 61.245(e)(3).

(13) ASTM E50-82, 86, 90 (Reapproved 1995), Standard Practices for Apparatus Reagents, and Safety Precautions for Chemical Analysis of Metals, IBR approved for Appendix B: Method 108C, Section 6.1.4.

\* \* \* \* \*

#### § 61.20 [Amended]

3. Amend § 61.20 as follows:

a. Paragraph (a) is amended by revising the words “100,000 tons” to read “90,720 megagrams (Mg) (100,000 tons).”

b. Paragraph (b) is amended by revising the words “10,000 tons” to read “9,072 Mg (10,000 tons).”

c. Paragraph (b) is amended by revising the words “100,000 tons” to read “90,720 Mg (100,000 tons).”

#### 61.21 [Amended]

4. In § 61.21(b), the words “Effective dose equivalent means the sum of the products of absorbed dose and appropriate factors to account for differences in biological effectiveness due to the quality of radiation and its distribution in the body of reference man” are revised to read “Effective dose equivalent means the sum of the products of the absorbed dose and appropriate effectiveness factors. These factors account for differences in biological effectiveness due to the quality of radiation and its distribution in the body of reference man.”

#### § 61.23 [Amended]

5. Amend § 61.23 as follows:

a. In paragraph (a), the first sentence is amended by revising the abbreviation “EPA” to read “U.S. Environmental Protection Agency (EPA).”

b. In paragraph (a), the second sentence is amended by revising the word “Appendix” to read “appendix.”

#### § 61.24 [Amended]

6. Amend § 61.24 as follows:

a. In paragraph (a), the first sentence is amended by revising the words “used in making the calculation” to read “used in making the calculations.”

b. In paragraph (a), the second sentence is amended by revising the words “Such report shall” to read “This report shall.”

#### § 61.30 [Amended]

7. In § 61.30, paragraph (a) is amended by revising the words “Extraction plans” to read “Extraction plants.”

#### § 61.32 [Amended]

8. Amend § 61.32 as follows:

a. Paragraph (a) is amended by revising the words “10 grams” to read “10 grams (0.022 lb).”

b. Paragraphs (b) and (b)(1)(i) are amended by revising the words “0.01  $\mu\text{g}/\text{m}^3$ ” to read “0.01  $\mu\text{g}/\text{m}^3$  (4.37 $\times 10^{-6}$   $\text{g}/\text{ft}^3$ )” wherever they occur.

#### § 61.42 [Amended]

9. Amend § 61.42 as follows:

a. Paragraph (a) is amended by revising the words “75 microgram minutes per cubic meter of air” to read “75 microgram minutes per cubic meter ( $\mu\text{g}\cdot\text{min}/\text{m}^3$ ) (4.68 pound minutes per cubic foot ( $\text{lb}\cdot\text{min}/\text{ft}^3$ )) of air.”

b. Paragraph (b) is amended by revising the words “2 grams per hour” to read “2.0 g/hr (0.0044 lb/hr).”

c. Paragraph (b) is amended by revising the words “10 grams per day” to read “10 g/day (0.022 lb/day).”

#### § 61.52 [Amended]

10. Amend § 61.52 as follows:

a. Paragraph (a) is amended by revising the words “2300 grams” to read “2.3 kg (5.1 lb).”

b. Paragraph (b) is amended by revising the words “3200 grams” to read “3.2 kg (7.1 lb).”

#### § 61.53 [Amended]

11. In § 61.53, paragraph (c) is amended by revising the words “1,300 gms/day” to read “1.3 kg/day (2.9 lb/day).”

#### § 61.55 [Amended]

12. Amend § 61.55 as follows:

a. In paragraph (a), the second sentence is amended by revising the words “1,600 g” to read “1.6 kg (3.5 lb).”

b. Paragraph (b)(1) is amended by revising the words “Reference Method” to read “Method” wherever they occur.

c. Paragraph (c)(4) is amended by revising the words “established in 2” to

read “established in paragraph (c)(2) of this section.”

#### § 61.61 [Amended]

13. Amend § 61.61 as follows:

a. Paragraph (c) is amended by revising the words “polyvinyl chloride plant” to read “polyvinyl chloride (PVC) plant.”

b. In paragraph (l), the first sentence is amended by revising the words “a least” to read “at least.”

c. Paragraph (w)(3) is amended by revising the words “Test Method 21” to read “Method 21.”

#### § 61.62 [Amended]

14. In § 61.62, paragraph (b) is amended by revising the words “0.2 g/kg (0.0002 lb/lb)” to read “0.2 g/kg (0.4 lb/ton).”

#### § 61.64 [Amended]

15. Amend § 61.64 as follows:

a. In paragraph (a)(2), the first sentence is amended by revising the words “0.02 g vinyl chloride/kg (0.00002 lb vinyl chloride/lb)” to read “0.02 g vinyl chloride/kg (0.04 lb vinyl chloride/ton).”

b. Paragraph (e)(2)(i) is amended by revising the words “2 g/kg (0.002 lb/lb)” to read “2 g/kg (4 lb/ton).”

c. Paragraph (e)(2)(ii) is amended by revising the words “0.4 g/kg (0.0004 lb/lb)” to read “0.4 g/kg (0.8 lb/ton).”

d. Paragraph (f)(2)(i) is amended by revising the words “2.02 g/kg (0.00202 lb/lb)” to read “2.02 g/kg (4.04 lb/ton).”

e. Paragraph (f)(2)(ii) is amended by revising the words “0.42 g/kg (0.00042 lb/lb)” to read “0.42 g/kg (0.84 lb/ton).”

#### § 61.65 [Amended]

16. Amend § 61.65 as follows:

a. In paragraph (a), the first sentence is amended by revising the words “*Relief valve discharge*” to read “*Relief valve discharge (RVD)*.”

b. Paragraph (b)(8)(i)(D)(1) is amended by revising the words “sections 5.2.1. and 5.2.2. of Test Method 106 and in accordance with section 7.1 of Test Method 106” to read “sections 7.2.1 and 7.2.2 of Method 106 and in accordance with section 10.1 of Method 106.”

c. In paragraph (b)(8)(i)(D)(2), the fourth sentence is amended by revising the words “maximum self life” to read “maximum shelf life.”

d. In paragraph (b)(8)(i)(D)(2), the fifth sentence is amended by revising the words “section 7.3 of Test Method 106. The requirements in section 5.2.3.1. and 5.2.3.2. of Test Method 106” to read “Sections 8.1 and 9.2 of Method 106. The requirements in Sections 7.2.3.1 and 7.2.3.2 of Method 106.”

e. In paragraph (c), the second sentence is amended by revising the

words "Test Method" to read "Method 106."

17. Amend § 61.67 by:

a. Revising § 61.67(g).

b. In paragraph (h)(1) by revising "ASTM Method D-2267" to read "ASTM D2267-68, 78, or 88 or D4420-94."

The revisions read as follows:

#### § 61.67 Emission tests.

\* \* \* \* \*

(g) Unless otherwise specified, the owner or operator shall use the test methods in Appendix B to this part for each test as required by paragraphs (g)(1), (g)(2), (g)(3), (g)(4), and (g)(5) of this section, unless an alternative method has been approved by the Administrator. If the Administrator finds reasonable grounds to dispute the results obtained by an alternative method, he may require the use of a reference method. If the results of the reference and alternative methods do not agree, the results obtained by the reference method prevail, and the Administrator may notify the owner or operator that approval of the method previously considered to be alternative is withdrawn. Whenever Method 107 is specified, and the conditions in Section 1.2, "Applicability" of Method 107A are met, Method 107A may be used.

(1) Method 106 is to be used to determine the vinyl chloride emissions from any source for which an emission limit is prescribed in § 61.62(a) or (b), § 61.63(a), or § 61.64(a)(1), (b), (c), or (d), or from any control system to which reactor emissions are required to be ducted in § 61.64(a)(2) or to which fugitive emissions are required to be ducted in § 61.65(b)(1)(ii), (b)(2), (b)(5), (b)(6)(ii), or (b)(9)(ii).

(i) For each run, one sample is to be collected. The sampling site is to be at least two stack or duct diameters downstream and one half diameter upstream from any flow disturbance such as a bend, expansion, contraction, or visible flame. For a rectangular cross section, an equivalent diameter is to be determined from the following equation:

$$\text{Equivalent diameter} = \frac{2(\text{length})(\text{width})}{(\text{length} + \text{width})}$$

The sampling point in the duct is to be at the centroid of the cross section. The sample is to be extracted at a rate proportional to the gas velocity at the sampling point. The sample is to contain a minimum volume of 50 liters (1.8 ft<sup>3</sup>) corrected to standard conditions and is to be taken over a period as close to 1 hour as practicable.

(ii) Each emission test is to consist of three runs. For the purpose of determining emissions, the average of results of all runs is to apply. The

average is to be computed on a time weighted basis.

(iii) For gas streams containing more than 10 percent oxygen, the concentration of vinyl chloride as determined by Method 106 is to be corrected to 10 percent oxygen (dry basis) for determination of emissions by using the following equation:

$$C_{b(\text{corrected})} = C_b (10.9)/(20.9 - \text{percent O}_2)$$

Where:

$C_{b(\text{corrected})}$  = The concentration of vinyl chloride in the exhaust gases, corrected to 10 percent oxygen.

$C_b$  = The concentration of vinyl chloride as measured by Method 106.

20.9 = Percent oxygen in the ambient air at standard conditions.

10.9 = Percent oxygen in the ambient air at standard conditions, minus the 10.0 percent oxygen to which the correction is being made.

Percent O<sub>2</sub> = Percent oxygen in the exhaust gas as measured by Method 3 of Appendix A of Part 60 of this chapter.

(iv) For those emission sources where the emission limit is prescribed in terms of mass rather than concentration, mass emissions are to be determined using the following equation:

$$C_{BX} = \frac{C_b D_{VC} Q K (10^{-6})}{Z}$$

Where:

$C_{BX}$  = Vinyl chloride emissions, g/kg (lb/lb) product.

$C_b$  = Concentration of vinyl chloride as measured by Test Method 106, ppmv.

$D_{VC}$  = Density of vinyl chloride at standard conditions, 2.60 kg/m<sup>3</sup> (0.162 lb/ft<sup>3</sup>).

$Q$  = Volumetric flow rate as determined by Method 2 of Appendix A to Part 60 of this chapter, m<sup>3</sup>/hr (ft<sup>3</sup>/hr).

$K$  = Unit conversion factor, 1,000 g/kg (1 lb/lb).

$10^{-6}$  = Conversion factor for ppm.

$Z$  = Production rate, kg/hr (lb/hr).

(2) Method 107 or Method 601 (incorporated by reference as specified in § 61.18) is to be used to determine the concentration of vinyl chloride in each inprocess wastewater stream for which an emission limit is prescribed in § 61.65(b)(9)(i).

(3) When a stripping operation is used to attain the emission limits in § 61.64(e) and (f), emissions are to be determined using Method 107 as follows:

(i) The number of strippers (or reactors used as strippers) and samples and the types and grades of resin to be sampled are to be determined by the

Administrator for each individual plant at the time of the test based on the plant's operation.

(ii) Each sample is to be taken immediately following the stripping operation.

(iii) The corresponding quantity of material processed by each stripper (or reactor used as a stripper) is to be determined on a dry solids basis and by a method submitted to and approved by the Administrator.

(iv) At the prior request of the Administrator, the owner or operator shall provide duplicates of the samples required in paragraph (g)(3)(i) of this section.

(4) Where control technology other than or in addition to a stripping operation is used to attain the emission limit in § 61.64(e), emissions are to be determined as follows:

(i) Method 106 is to be used to determine atmospheric emissions from all of the process equipment simultaneously. The requirements of paragraph (g)(1) of this section are to be met.

(ii) Method 107 is to be used to determine the concentration of vinyl chloride in each inprocess wastewater stream subject to the emission limit prescribed in § 61.64(e). Vinyl chloride mass emissions are to be determined using the following equation:

$$C_{BX} = \frac{C_{rv} Q_{\text{water}} D_{\text{water}} Q K (10^{-6})}{Z}$$

Where:

$C_{BX}$  = Vinyl chloride emissions, g/kg (lb/lb) product in each inprocess wastewater stream.

$C_{rv}$  = Concentration of vinyl chloride in wastewater, as measured by Method 107, ppmw.

$D_{\text{water}}$  = Density of wastewater, 1.0 kg/m<sup>3</sup> (0.0624 lb/ft<sup>3</sup>).

$Q_{\text{water}}$  = Wastewater flow rate, determined in accordance with a method which has been submitted to and approved by the Administrator, m<sup>3</sup>/hr (ft<sup>3</sup>/hr).

$K$  = Unit conversion factor, 1,000 g/kg (1 lb/lb).

$10^{-6}$  = Conversion factor for ppm.

$Z$  = Production rate, kg/hr (lb/hr), determined in accordance with a method which has been submitted to and approved by the Administrator.

(5) The reactor opening loss for which an emission limit is prescribed in § 61.64(a)(2) is to be determined. The number of reactors for which the determination is to be made is to be specified by the Administrator for each individual plant at the time of the

determination based on the plant's operation.

(i) Except as provided in paragraph (g)(5)(ii) of this section, the reactor opening loss is to be determined using the following equation:

$$C_{BX} = C_b \frac{V_R D_{VC} Q K (10^{-6})}{Z}$$

Where:

$C_{BX}$  = Vinyl chloride emissions, g/kg (lb/lb) product.

$C_b$  = Concentration of vinyl chloride, in ppmv, as determined by Method 106 or a portable hydrocarbon detector which measures hydrocarbons with a sensitivity of at least 10 ppmv.

$V_R$  = Capacity of the reactor, m<sup>3</sup> (ft<sup>3</sup>).

$D_{VC}$  = Density of vinyl chloride at standard conditions, 2.60 kg/m<sup>3</sup> (0.162 lb/ft<sup>3</sup>).

$K$  = Unit conversion factor, 1,000 g/kg (1 lb/lb).

$10^{-6}$  = Conversion factor for ppm.

$Z$  = Production rate, kg/hr (lb/hr).

(A) If Method 106 is used to determine the concentration of vinyl chloride ( $C_b$ ), the sample is to be withdrawn at a constant rate with a probe of sufficient length to reach the vessel bottom from the manhole.

Samples are to be taken for 5 minutes within 6 inches of the vessel bottom, 5 minutes near the vessel center, and 5 minutes near the vessel top.

(B) If a portable hydrocarbon detector is used to determine the concentration of vinyl chloride ( $C_b$ ), a probe of sufficient length to reach the vessel bottom from the manhole is to be used to make the measurements. One measurement will be made within 6 inches of the vessel bottom, one near the vessel center and one near the vessel top. Measurements are to be made at each location until the reading is stabilized. All hydrocarbons measured are to be assumed to be vinyl chloride.

(C) The production rate of polyvinyl chloride ( $Z$ ), which is the product of the average batch weight and the number of batches produced since the reactor was last opened to the atmosphere, is to be determined by a method submitted to and approved by the Administrator.

(ii) A calculation based on the number of evacuations, the vacuum involved, and the volume of gas in the reactor is hereby approved by the Administrator as an alternative method for determining reactor opening loss for postpolymerization reactors in the manufacture of bulk resins. Calculation methods based on techniques other than repeated evacuation of the reactor may

be approved by the Administrator for determining reactor opening loss for postpolymerization reactors in the manufacture of bulk resins.

(6) For a reactor that is used as a stripper, the emissions of vinyl chloride from reactor opening loss and all sources following the reactor used as a stripper for which an emission limit is prescribed in § 61.64(f) are to be determined. The number of reactors for which the determination is to be made is to be specified by the Administrator for each individual plant at the time of the determination based on the plant's operation.

(i) For each batch stripped in the reactor, the following measurements are to be made:

(A) The concentration of vinyl chloride in resin after stripping, measured according to paragraph (g)(3) of this section;

(B) The reactor vacuum at end of strip from plant instrument; and

(C) The reactor temperature at the end of strip from plant instrument.

(ii) For each batch stripped in the reactor, the following information is to be determined:

(A) The vapor pressure of water in the reactor at the end of strip from the following table:

#### METRIC UNITS

Reactor vapor temperature (°C)	H <sub>2</sub> O vapor pressure (mm Hg)	Reactor vapor temperature (°C)	H <sub>2</sub> O vapor pressure (mm Hg)	Reactor vapor temperature (°C)	H <sub>2</sub> O vapor pressure (mm Hg)
40	55.3	62	163.8	84	416.8
41	58.3	63	171.4	85	433.6
42	61.5	64	179.3	86	450.9
43	64.8	65	187.5	87	468.7
44	68.3	66	196.1	88	487.1
45	71.9	67	205.0	89	506.1
46	75.6	68	214.2	90	525.8
47	79.6	69	223.7	91	546.0
48	83.7	70	233.7	92	567.0
49	88.0	71	243.9	93	588.6
50	92.5	72	254.6	94	610.9
51	97.2	73	265.7	95	633.9
52	102.1	74	277.2	96	657.6
53	107.2	75	289.1	97	682.1
54	112.5	76	301.4	98	707.3
55	118.0	77	314.1	99	733.2
56	123.8	78	327.3	100	760.0
57	129.8	79	341.0		
58	136.1	80	355.1		
59	142.6	81	369.7		
60	149.4	82	384.9		
61	156.4	83	400.6		

## ENGLISH UNITS

Reactor vapor temperature (°F)	H <sub>2</sub> O vapor pressure (psia)	Reactor vapor temperature (°F)	H <sub>2</sub> O vapor pressure (psia)	Reactor vapor temperature (°F)	H <sub>2</sub> O vapor pressure (psia)
104	1.07	144	3.167	183	8.060
106	1.13	145	3.314	185	8.384
108	1.19	147	3.467	187	8.719
109	1.25	149	3.626	189	9.063
111	1.32	151	3.792	190	9.419
113	1.39	153	3.964	192	9.786
115	1.46	154	4.142	194	10.17
117	1.54	156	4.326	196	10.56
118	1.62	158	4.519	198	10.96
120	1.70	160	4.716	199	11.38
122	1.79	162	4.923	201	11.81
124	1.88	163	5.138	203	12.26
126	1.974	165	5.360	205	12.72
127	2.073	167	5.590	207	13.19
129	2.175	169	5.828	208	13.68
131	2.282	170	6.074	210	14.18
133	2.394	172	6.329	212	14.70
135	2.510	174	6.594		
136	2.632	176	6.866		
138	2.757	178	7.149		
140	2.889	180	7.443		
142	3.024	181	7.746		

(B) The partial pressure of vinyl chloride in reactor at end of strip from the following equation:

$$PP_{VC} = P_{ATM} - P_{RV} - P_W$$

Where:

$PP_{VC}$  = Partial pressure of vinyl chloride, mm Hg (psia)  
 $P_{ATM}$  = Atmospheric pressure at 0 °C (32 °F), 760 mm Hg (14.7 psia)  
 $P_{RV}$  = Absolute pressure of reactor vacuum, mm Hg (psia)  
 $P_W$  = Vapor pressure of water, mm Hg (psia)

(C) The reactor vapor space volume at the end of the strip from the following equation:

$$V_{RVS} = V_R - V_W - \frac{W_{PVC}}{D_{PVC}}$$

Where:

$V_{RVS}$  = Reactor vapor space volume, m<sup>3</sup> (ft<sup>3</sup>)  
 $V_R$  = Reactor capacity, m<sup>3</sup> (ft<sup>3</sup>)  
 $V_W$  = Volume of water in reactor from recipe, m<sup>3</sup> (ft<sup>3</sup>)  
 $W_{PVC}$  = Dry weight of polyvinyl chloride in reactor from recipe, kg (lb)  
 $D_{PVC}$  = Typical density of polyvinyl chloride, 1,400 kg/m<sup>3</sup> (87.4 lb/ft<sup>3</sup>)

(iii) For each batch stripped in the reactor, the combined reactor opening loss and emissions from all sources following the reactor used as a stripper is to be determined using the following equation:

$$C_{BX} = K_1 (PPM_{VC}) + \frac{(PP_{VC})(V_{RVS})(R_{VC})}{(M_{VC})(T_R + K_T)}$$

Where:

$C_{BX}$  = Vinyl chloride emissions, g/kg (lb/lb) product.  
 $PPM_{VC}$  = Concentration of vinyl chloride in resin after stripping, ppmw  
 $K_1$  = Conversion factor from ppmw to units of emission standard, 0.001 (metric units) = 0.002 (English units)  
 $PP_{VC}$  = Partial pressure of vinyl chloride determined according to paragraph (g)(6)(ii)(B) of this section, mm Hg (psia)  
 $V_{RVS}$  = Reactor vapor space volume determined according to paragraph (g)(6)(ii)(C) of this section, m<sup>3</sup> (ft<sup>3</sup>)

$R_{VC}$  = Ideal gas constant for vinyl chloride, 1,002 g-°K/(mm Hg-m<sup>3</sup>) [5.825 lb-°R/(psia-ft<sup>3</sup>)]  
 $M_{PVC}$  = Dry weight of polyvinyl chloride in reactor from recipe, kg (lb)  
 $T_R$  = Reactor temperature, °C (°F)  
 $K_T$  = Temperature conversion factor for °C to °K, 273 (°F to °R, 460)

(h)(1) Each piece of equipment within a process unit that can reasonably contain equipment in vinyl chloride service is presumed to be in vinyl chloride service unless an owner or operator demonstrates that the piece of equipment is not in vinyl chloride service. For a piece of equipment to be

considered not in vinyl chloride service, it must be determined that the percent vinyl chloride content can be reasonably expected not to exceed 10 percent by weight for liquid streams or contained liquid volumes and 10 percent by volume for gas streams or contained gas volumes, which also includes gas volumes above liquid streams or contained liquid volumes. For purposes of determining the percent vinyl chloride content of the process fluid that is contained in or contacts equipment, procedures that conform to the methods described in ASTM Method D-2267 (incorporated by

reference as specified in § 61.18) shall be used.

(2)(i) An owner or operator may use engineering judgment rather than the procedures in paragraph (h)(1) of this section to demonstrate that the percent vinyl chloride content does not exceed 10 percent by weight for liquid streams and 10 percent by volume for gas streams, provided that the engineering judgment demonstrates that the vinyl chloride content clearly does not exceed 10 percent. When an owner or operator and the Administrator do not agree on whether a piece of equipment is not in vinyl chloride service, however, the procedures in paragraph (h)(1) of this section shall be used to resolve the disagreement.

(ii) If an owner or operator determines that a piece of equipment is in vinyl chloride service, the determination can be revised only after following the procedures in paragraph (h)(1) of this section.

(3) Samples used in determining the percent vinyl chloride content shall be representative of the process fluid that is contained in or contacts the equipment.

#### § 61.68 [Amended]

18. Amend § 61.68 as follows:

a. Paragraph (c)(1) is amended by revising the words "sections 5.2.1. and 5.2.2. of Test Method 106 and in accordance with section 7.1 of Test Method 106" to read "Sections 7.2.1 and 7.2.2 of Method 106 and in accordance with Section 10.1 of Method 106."

b. In paragraph (c)(2), the fifth sentence is amended by revising the words "section 7.3 of Test Method 106. The requirements in section 5.2.3.1. and 5.2.3.2. of Test Method 106" to read "Sections 8.1 and 9.2 of Method 106. The requirements in Sections 7.2.3.1 and 7.2.3.2 of Method 106."

19. § 61.70(c) is revised as follows:  
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#### § 61.70 Reporting.

\* \* \* \* \*

(c) Unless otherwise specified, the owner or operator shall use the test methods in Appendix B to this part to conduct emission tests as required by paragraphs (c)(2) and (c)(3) of this section, unless an alternative method has been approved by the Administrator. If the Administrator finds reasonable grounds to dispute the results obtained by an alternative method, he may require the use of a reference method. If the results of the reference and alternative methods do not agree, the results obtained by the reference method prevail, and the Administrator may notify the owner or operator that approval of the method previously considered to be alternative is withdrawn.

(1) The owner or operator shall include in the report a record of the vinyl chloride content of emissions for each 3-hour period during which average emissions are in excess of the emission limits in § 61.62(a) or (b), § 61.63(a), or § 61.64(a)(1), (b), (c), or (d), or during which average emissions are in excess of the emission limits specified for any control system to which reactor emissions are required to be ducted in § 61.64(a)(2) or to which fugitive emissions are required to be ducted in § 61.65(b)(1)(ii), (b)(2), (b)(5), (b)(6)(ii), or (b)(9)(ii). The number of 3-hour periods for which average emissions were determined during the reporting period shall be reported. If emissions in excess of the emission limits are not detected, the report shall contain a statement that no excess emissions have been detected. The emissions are to be determined in accordance with § 61.68(e).

(2) In polyvinyl chloride plants for which a stripping operation is used to attain the emission level prescribed in § 61.64(e), the owner or operator shall include in the report a record of the

vinyl chloride content in the polyvinyl chloride resin.

(i) If batch stripping is used, one representative sample of polyvinyl chloride resin is to be taken from each batch of each grade of resin immediately following the completion of the stripping operation, and identified by resin type and grade and the date and time the batch is completed. The corresponding quantity of material processed in each stripper batch is to be recorded and identified by resin type and grade and the date and time the batch is completed.

(ii) If continuous stripping is used, one representative sample of polyvinyl chloride resin is to be taken for each grade of resin processed or at intervals of 8 hours for each grade of resin which is being processed, whichever is more frequent. The sample is to be taken as the resin flows out of the stripper and identified by resin type and grade and the date and time the sample was taken. The corresponding quantity of material processed by each stripper over the time period represented by the sample during the 8-hour period, is to be recorded and identified by resin type and grade and the date and time it represents.

(iii) The vinyl chloride content in each sample is to be determined by Method 107 as prescribed in § 61.67(g)(3).

(iv) [Reserved]

(v) The report to the Administrator by the owner or operator is to include a record of any 24-hour average resin vinyl chloride concentration, as determined in this paragraph, in excess of the limits prescribed in § 61.64(e). The vinyl chloride content found in each sample required by paragraphs (c)(2)(i) and (c)(2)(ii) of this section shall be averaged separately for each type of resin, over each calendar day and weighted according to the quantity of each grade of resin processed by the stripper(s) that calendar day, according to the following equation:

$$A_T = \frac{\sum_{i=1}^n P_{Gi} M_{Gi}}{Q_T} = \frac{P_{G1} M_{G1} + P_{G2} M_{G2} + \dots + P_{Gn} M_{Gn}}{Q_T}$$

Where:

$A_T$  = 24-hour average concentration of type T resin in ppm (dry weight basis).

$Q_T$  = Total production of type T resin over the 24-hour period, in kg (ton).

T = Type of resin.

$M_{Gi}$  = Concentration of vinyl chloride in one sample of grade  $G_i$  resin in ppm.

$P_{Gi}$  = Production of grade  $G_i$  resin represented by the sample, in kg (ton).

$G_i$  = Grade of resin: e.g.,  $G_1$ ,  $G_2$ ,  $G_3$ .

n = Total number of grades of resin produced during the 24-hour period.

The number of 24-hour average concentrations for each resin type determined during the reporting period shall be reported. If no 24-hour average resin vinyl chloride concentrations in excess of the limits prescribed in

§ 61.64(e) are measured, the report shall state that no excess resin vinyl chloride concentrations were measured.

(vi) The owner or operator shall retain at the source and make available for inspection by the Administrator for a minimum of 3 years records of all data needed to furnish the information required by paragraph (c)(2)(v) of this section. The records are to contain the following information:

(A) The vinyl chloride content found in all the samples required in paragraphs (c)(2)(i) and (c)(2)(ii) of this section, identified by the resin type and grade and the time and date of the sample, and

(B) The corresponding quantity of polyvinyl chloride resin processed by the stripper(s), identified by the resin type and grade and the time and date it represents.

(3) The owner or operator shall include in the report a record of any emissions from each reactor opening in excess of the emission limits prescribed in § 61.64(a)(2). Emissions are to be determined in accordance with

§ 61.67(g)(5), except that emissions for each reactor are to be determined. The number of reactor openings during the reporting period shall be reported. If emissions in excess of the emission limits are not detected, the report shall include a statement that excess emissions have not been detected.

(4) In polyvinyl chloride plants for which stripping in the reactor is used to attain the emission level prescribed in § 61.64(f), the owner or operator shall include in the report a record of the vinyl chloride emissions from reactor opening loss and all sources following the reactor used as a stripper.

(i) One representative sample of polyvinyl chloride resin is to be taken from each batch of each grade of resin immediately following the completion of the stripping operation, and identified by resin type and grade and the date and time the batch is completed. The corresponding quantity of material processed in each stripper batch is to be recorded and identified by resin type and grade and the date and time the batch is completed.

(ii) The vinyl chloride content in each sample is to be determined by Method 107 as prescribed in § 61.67(g)(3).

(iii) The combined emissions from reactor opening loss and all sources following the reactor used as a stripper are to be determined for each batch stripped in a reactor according to the procedure prescribed in § 61.67(g)(6).

(iv) The report to the Administrator by the owner or operator is to include a record of any 24-hour average combined reactor opening loss and emissions from all sources following the reactor used as a stripper as determined in this paragraph, in excess of the limits prescribed in § 61.64(f). The combined reactor opening loss and emissions from all sources following the reactor used as a stripper associated with each batch are to be averaged separately for each type of resin, over each calendar day and weighted according to the quantity of each grade of resin stripped in reactors that calendar day as follows:

For each type of resin (suspension, dispersion, latex, bulk, other), the following calculation is to be performed:

$$A_T = \frac{\sum_{i=1}^n P_{Gi} C_{Gi}}{Q_T} = \frac{P_{G1} C_{G1} + P_{G2} C_{G2} + \dots + P_{Gn} C_{Gn}}{Q_T}$$

Where:

$A_T$  = 24-hour average combined reactor opening loss and emissions from all sources following the reactor used as a stripper, in g vinyl chloride/kg (lb/ton) product (dry weight basis).

$Q_T$  = Total production of resin in batches for which stripping is completed during the 24-hour period, in kg (ton).

$T$  = Type of resin.

$C_{Gi}$  = Average combined reactor opening loss and emissions from all sources following the reactor used as a stripper of all batches of grade  $G_i$  resin for which stripping is completed during the 24-hour period, in g vinyl chloride/kg (lb/ton) product (dry weight basis) (determined according to procedure prescribed in § 61.67(g)(6)).

$P_{Gi}$  = Production of grade  $G_i$  resin in the batches for which  $C$  is determined, in kg (ton).

$G_i$  = Grade of resin: e.g.,  $G_1$ ,  $G_2$ ,  $G_3$ .

$n$  = Total number of grades of resin in batches for which stripping is completed during the 24-hour period.

The number of 24-hour average emissions determined during the reporting period shall be reported. If no

24-hour average combined reactor opening loss and emissions from all sources following the reactor used as a stripper in excess of the limits prescribed in § 61.64(f) are determined, the report shall state that no excess vinyl chloride emissions were determined.

\* \* \* \* \*

#### § 61.93 [Amended]

20. In § 61.93, paragraphs (b)(1)(I), (b)(1)(ii), and (b)(2)(I) are amended by revising the words "Reference Method" to read "Method" wherever they occur.

#### § 61.107 [Amended]

21. Amend § 61.107 as follows:

a. Paragraphs (b)(1)(I), (b)(1)(ii), and (b)(2)(I) are amended by revising the words "Reference Method" to read "Method" wherever they occur.

b. Paragraphs (b)(2)(iv) and (b)(5)(v) are amended by revising the words "method 114" to read "Method 114" wherever they occur.

c. Paragraph (b)(5)(iv) is amended by revising the words "table 2" to read "Table 2", wherever they occur.

#### § 61.110 [Amended]

22. In § 61.110, paragraph (c)(2) is amended by revising the words "1,000 megagrams" to read "1,000 megagrams (1,102 tons)."

#### § 61.123 [Amended]

23. Amend § 61.123 as follows:

a. Paragraph (d) is amended by revising the words "curies per metric ton" to read "curies per Mg or curies per ton" wherever they occur.

b. In paragraph (d), the fifth sentence is amended by revising the words "in metric tons" to read "in Mg (tons)."

#### § 61.125 [Amended]

24. Amend § 61.125 as follows:

a. Paragraph (a)(1) is amended by revising the words "Test Method 1 of Appendix A" to read "Method 1 of Appendix A."

b. Paragraph (a)(2) is amended by revising the words "Test Method 2 of Appendix A" to read "Method 2 of Appendix A."

c. Paragraph (a)(3) is amended by revising the words "Test Method 3 of Appendix A" to read "Method 3 of Appendix A."

d. Paragraph (a)(4) is amended by revising the words "Test Method 5 of

Appendix A” to read “Method 5 of Appendix A.”

e. Paragraph (a)(5) is amended by revising the words “Test Method 111 of Appendix B” to read “Method 111 of Appendix B.”

#### § 61.132 [Amended]

25. In § 61.132, paragraphs (b) and (b)(1) are amended by revising the words “Reference Method” to read “Method” wherever they occur.

#### § 61.133 [Amended]

26. In § 61.133, paragraphs (c) and (c)(1) are amended by revising the words “Reference Method” to read “Method” wherever they occur.

27. Amend § 61.139 as follows:

a. In paragraph (c)(1), the equation definitions for “ $Q_{aj}$ ” and “ $Q_{bi}$ ” are revised.

b. Paragraph (d)(2)(ii) is amended by revising the words “method 21” to read “Method 21” wherever they occur.

c. In paragraph (g)(1)(vi), the second sentence is amended by revising the words “Either follow section 7.1, “Integrated Bag Sampling and Analysis,” or section 7.2, “Direct Interface Sampling and Analysis Procedure”” to read “Either the integrated bag sampling and analysis procedure or the direct interface procedure may be used.”

d. Paragraph (g)(1)(vi)(A) is amended by revising the words “section 7.1” to read “the integrated bag sampling and analysis procedure.”

e. In paragraph (g)(1)(vi)(B), the first sentence is amended by revising the words “section 7.2” to read “the direct

interface sampling and analysis procedure.”

f. Paragraphs (h)(3), (h)(3)(ii), and (h)(4)(ii) are amended by revising the words “method 18” to read “Method 18” wherever they occur.

The revisions read as follows:

#### § 61.139 Provisions for alternative means for process vessels, storage tanks, and tar-intercepting sumps.

\* \* \* \* \*

(c) \* \* \*

(1) \* \* \*

$Q_{aj}$  = volumetric flow rate in vents after the control device, standard cubic meters/minute (scm/min) [standard cubic feet/minute (scf/min)].

$Q_{bi}$  = volumetric flow rate in vents before the control device, scm/min (scf/min).

\* \* \* \* \*

#### 61.155 [Amended]

28. In § 61.155, the section heading is amended by revising the words “asbestos-containing” to read “asbestos-containing.”

#### § 61.162 [Amended]

29. Amend § 61.162 as follows:

a. Paragraph (a)(1) is amended by revising the words “2.5 Mg per year” to read “2.5 Mg (2.7 ton) per year.”

b. Paragraph (b)(1) is amended by revising the words “0.4 Mg per year” to read “0.4 Mg (0.44 ton) per year.”

30. Amend § 61.164 as follows:

a. Paragraph (c) is amended by revising the words “8.0 Mg per year” to read “8.0 Mg (8.8 ton) per year.”

b. Paragraph (c) is amended by revising the words “1.0 Mg per year” to read “1.0 Mg (1.1 ton) per year.”

c. In paragraph (c)(1), the first sentence is amended by revising the words “grams of elemental arsenic per kilogram” to read “grams of elemental arsenic per kilogram (pounds per ton).”

d. Paragraphs (c)(1) and (d)(3) are revised; the equation and definitions in paragraphs (c)(2) and (d)(5) are revised; and the definitions of the terms “ $R_a$ ” and “ $T_i$ ” in paragraph (d)(4) are revised.

e. Paragraph (d) is amended by revising the words “8.0 Mg per year” to read “8.0 Mg (8.8 ton) per year.”

f. Paragraph (d) is amended by revising the words “1.0 Mg per year” to read “1.0 Mg (1.1 ton) per year.”

g. Paragraph (d)(2)(i) is amended by revising the words “emission rate (g/h)” to read “emission rate, g/hr (lb/hr).”

h. Paragraph (d)(2)(ii)(D) is amended by revising the words “Section 4 of Method 5D” to read “Section 8.0 of Method 5D.”

i. Paragraph (e)(1)(ii)(D) is amended by revising the words “Section 4 of Method 5D” to read “Section 8.0 of Method 5D.”

The revisions read as follows:

#### § 61.164 Test methods and procedures.

\* \* \* \* \*

(c) \* \* \*

(1) Derive a theoretical uncontrolled arsenic emission factor ( $T_i$ ), based on material balance calculations for each arsenic-containing glass type (i) produced during the 12-month period, as follows:

$$T_i = (A_{bi} \times W_{bi}) + (A_{ci} \times W_{ci}) - B_{gi}$$

Where:

$T_i$  = The theoretical uncontrolled arsenic emission factor for each glass type (i), g/kg (lb/ton).

$A_{bi}$  = Fraction by weight of elemental arsenic in the fresh batch for each glass type (i).

$W_{bi}$  = Weight of fresh batch melted per unit weight of glass produced for each glass type (i), g/kg (lb/ton).

$A_{ci}$  = Fraction by weight of elemental arsenic in cullet for each glass type (i).

$W_{ci}$  = Weight of cullet melted per unit weight of glass produced for each glass type (i), g/kg (lb/ton).

$B_{gi}$  = Weight of elemental arsenic per unit weight of glass produced for each glass type (i), g/kg (lb/ton).

(2) \* \* \*

$$Y_i = \frac{T_i G_i}{K}$$

Where:

$Y_i$  = Theoretical uncontrolled arsenic emission estimate for the 12-month period for each glass type, Mg/year (ton/year).

$T_i$  = Theoretical uncontrolled arsenic emission factor for each type of glass (i) produced during the 12-

month period as calculated in paragraph (c)(1) of this section, g/kg (lb/ton).

$G_i$  = Quantity of each arsenic-containing glass type (i) produced during the 12-month period, kg/yr (ton/yr).

$K$  = conversion factor for unit consistency,  $10^6$  g/Mg (2,000 lb/ton).

\* \* \* \* \*

(d) \* \* \*

(3) Determine the actual uncontrolled arsenic emission factor ( $R_a$ ) as follows:

$$R_a = E_a \div P$$

Where:

$R_a$  = Actual uncontrolled arsenic emission factor, g/kg (lb/ton).

$E_a$  = Actual uncontrolled arsenic emission rate from paragraph (d)(2) of this section, g/hr (lb/hr).

$P$  = Rate of glass production, kg/hr (ton/hr), determined by dividing the weight of glass pulled from the furnace during the emission test by the number of hours taken to perform the test under paragraph (d)(2) of this section.

(4) \* \* \*

$R_a$  = Actual uncontrolled arsenic emission factor, determined in paragraph (d)(3) of this section, g/kg (lb/ton).

$T_i$  = Theoretical uncontrolled arsenic emission factor, g/kg (lb/ton), determined in paragraph (c)(1) of this section for the same glass type for which  $R_a$  was determined.

(5) \* \* \*

$$U = \frac{\sum_{i=1}^n (T_i \times F \times G_i)}{K}$$

Where:

$U$  = Uncontrolled arsenic emission rate for the 12-month period, Mg/yr (ton/yr).

$T_i$  = Theoretical uncontrolled arsenic emission factor for each type of glass (i) produced during the 12-month period as calculated in paragraph (c)(1) of this section, g/kg (lb/ton).

$F$  = The correction factor calculated in paragraph (d)(4) of this section.

$G_i$  = Quantity of each arsenic-containing glass type (i) produced during the 12-month period, kg/yr (ton/yr).

$n$  = Number of arsenic-containing glass types produced during the 12-month period.

$K$  = Conversion factor for unit consistency,  $10^6$  g/Mg (2,000 lb/ton).

\* \* \* \* \*

#### § 61.165 [Amended]

31. In § 61.165, paragraph (a)(7) is amended by revising the words “all records of maintenance” at the beginning of the sentence to read “All maintenance.”

#### § 61.172 [Amended]

32. Amend § 61.172 as follows:

a. Paragraph (a) is amended by revising the words “75 kg/h” to read “75 kg/hr (165 lb/hr).”

b. Paragraph (c) is amended by revising the words “11.6 milligrams per dry standard cubic meter” to read “11.6 mg/dscm (0.0051 gr/dscf).”

#### § 61.174 [Amended]

33. In § 61.174, paragraph (f)(3) is amended by revising the equation definitions as follows:

#### § 61.174 Test methods and procedures.

\* \* \* \* \*

(f) \* \* \*

(3) \* \* \*

$R_c$  is the converter arsenic charging rate, kg/hr (lb/hr).

$A_c$  is the monthly average weight percent of arsenic in the copper matte charged during the month(%) as determined under paragraph (f)(2) of this section.

$A_l$  is the monthly average weight percent of arsenic in the lead matte charged during the month(%) as determined under paragraph (f)(2) of this section.

$W_{ci}$  is the total rate of copper matte charged to a copper converter during the month, kg (lb).

$W_{li}$  is the total rate of lead matte charged to a copper converter during the month, kg (lb).

$H_c$  is the total number of hours the copper converter department was in operation during the month (hr).

$n$  is the number of copper converters in operation during the month.

\* \* \* \* \*

#### § 61.192 [Amended]

34. In § 61.192, the first sentence is amended by revising the words “20 pCi/m<sup>2</sup>-s” to read “20 picocuries per square meter per second (pCi/(m<sup>2</sup>-sec)) (1.9 pCi/(ft<sup>2</sup>-sec)).”

#### § 61.202 [Amended]

35. In § 61.202, the third sentence is amended by revising the words “20 pCi/m<sup>2</sup>-s” to read “20 pCi/(m<sup>2</sup>-sec) (1.9 pCi/(ft<sup>2</sup>-sec)).”

#### § 61.204 [Amended]

36. In § 61.204, paragraph (b) is amended by revising the words “10 picocuries per gram (pCi/g)” to read “10 pCi/g (4500 pCi/lb).”

#### § 61.205 [Amended]

37–38. In § 61.205, paragraph (b)(2) is amended by revising the words “7,000 pounds” to read “3182 kg (7,000 lb)” wherever they occur.

#### § 61.208 [Amended]

39. Amend § 61.208 as follows:

a. Paragraph (a)(1)(iii) is amended by revising the words “quantity (in pounds) of phosphogypsum” are revised to read “quantity of phosphogypsum, in kilograms or pounds.”

b. Paragraph (a)(1)(vi) is amended by revising the words “in pCi/g” to read “in pCi/g (pCi/lb).”

#### § 61.222 [Amended]

40. In § 61.222, paragraph (a) is amended by revising the words “20 pCi/m<sup>2</sup>-s” to read “20 pCi/(m<sup>2</sup>-sec) (1.9 pCi/(ft<sup>2</sup>-sec)).”

#### § 61.241 [Amended]

41. In § 61.241, the definition of the term “In vacuum service” is amended by revising the words “5 kilopascals (kPa) below” to read “5 kilopascals (kPa) (0.7 psia) below.”

#### § 61.242–11 [Amended]

42. In § 61.242–11, paragraph (c) is amended by revising the words “760 °C” to read “760 °C (1,400 °F).”

#### § 61.243–2 [Amended]

43. Amend § 61.243–2 as follows:

a. Paragraph (b)(2) is amended by revising the words “skip 1 of the” to read “skip one of the.”

b. Paragraph (b)(3) is amended by revising the words “After 5 consecutive” to read “After five consecutive.”

c. Paragraph (b)(3) is amended by revising the words “skip 3 of the quarterly” to read “skip three of the quarterly.”

#### § 61.244 [Amended]

44. Amend § 61.244 as follows:

a. In paragraph (b)(1) by revising the words “emission limitation.limitation to test data” to read “emission limitation to test data.”

b. By redesignating paragraph (b)(3) as paragraph (b)(2).

#### § 61.245 [Amended]

45–46. Amend § 61.245 as follows:

a. Paragraphs (b)(2), (b)(3), (b)(5), (c)(2), (c)(3), (e)(3), and (e)(4) are amended by revising the words “Reference Method” to read “Method” wherever they occur.

b. In paragraph (e)(3), the definitions of the terms “ $H_T$ ”, “ $K$ ”, “ $C_i$ ”, and “ $H_i$ ” are revised; and the equation and definitions in (e)(5) are revised as follows:

**§ 61.245 Test methods and procedures.**

\* \* \* \* \*

- (e) \* \* \*  
(3) \* \* \*

$H_T$  = Net heating value of the sample, MJ/scm (BTU/scf); where the net enthalpy per mole of offgas is based on combustion at 25 °C and 760 mm Hg (77 °F and 14.7 psi), but the standard temperature for determining the volume corresponding to one mole is 20 °C (68 °F).

$K$  = conversion constant,  $1.740 \times 10^{-7}$  (g-mole) (MJ)/(ppm-scm-kcal) (metric units); or  $4.674 \times 10^8$  (g-mole) (Btu)/(ppm-scf-kcal) (English units)

$C_i$  = Concentration of sample component "i" in ppm, as measured by Method 18 of Appendix A to 40 CFR Part 60 and ASTM D2504-67, 77, or 88 (Reapproved 1993) (incorporated by reference as specified in § 61.18).

$H_i$  = net heat of combustion of sample component "i" at 25 °C and 760 mm Hg (77 °F and 14.7 psi), kcal/g-mole. The heats of combustion may be determined using ASTM D2382-76 or 88 or D4809-95 (incorporated by reference as specified in § 61.18) if published values are not available or cannot be calculated.

\* \* \* \* \*

- (5) \* \* \*

$$V_{\max} = K_1 + K_2 H_T$$

Where:

$V_{\max}$  = Maximum permitted velocity, m/sec (ft/sec).

$H_T$  = Net heating value of the gas being combusted, as determined in paragraph (e)(3) of this section, MJ/scm (Btu/scf).

$K_1$  = 8.706 m/sec (metric units)  
= 28.56 ft/sec (English units)

$K_2$  = 0.7084 m<sup>4</sup>/(MJ-sec) (metric units)  
= 0.087 ft<sup>4</sup>/(Btu-sec) (English units)

\* \* \* \* \*

**§ 61.252 [Amended]**

47. In § 61.252, paragraph (a) is amended by revising the words "20 pCi/m<sup>2</sup>-s" to read "20 pCi/(m<sup>2</sup>-sec) (1.9 pCi/(ft<sup>2</sup>-sec))."

**§ 61.270 [Amended]**

48. Amend § 61.270 as follows:

a. Paragraph (a) is revised.

b. Paragraph (e) is amended by revising the words "204.9 kPa" to read "204.9 kPa (29.72 psia)."

The revisions read as follows:

**§ 61.270 Applicability and designation of sources.**

(a) The source to which this subpart applies is each storage vessel that is

storing benzene having a specific gravity within the range of specific gravities specified in ASTM D836-84 for Industrial Grade Benzene, ASTM D835-85 for Refined Benzene-485, ASTM D2359-85a or 93 for Refined Benzene-535, and ASTM D4734-87 or 96 for Refined Benzene-545. These specifications are incorporated by reference as specified in § 61.18. See § 61.18 for acceptable versions of these methods.

\* \* \* \* \*

**§ 61.272 [Amended]**

49. Amend § 61.272 as follows:

a. In paragraph (c)(1)(i), the fourth sentence is amended by revising the words "816 °C" to read "816 °C (1,500 °F)."

b. Paragraph (d) is amended by revising the letter "O" in the words "40 CFR 60.18(e)" to read "40 CFR 60.18(e)."

**§ 61.301 [Amended]**

50. Amend § 61.301 as follows:

a. The definitions of the terms "Leak" and "Vapor-tight marine vessel" are amended by revising the words "method 21" to read "Method 21" wherever they occur.

b. In the definition of the terms "Vapor-tight tank truck or vapor-tight railcar", the second sentence is amended by revising the words "method 27 of part 60, appendix A" to read "Method 27 of Appendix A to 40 CFR part 60."

**§ 61.302 [Amended]**

51. Amend § 61.302 as follows:

a. In paragraph (d)(1), the third sentence is amended by revising the words "method 27 of part 60, appendix A" to read "Method 27 of Appendix A to 40 CFR Part 60."

b. In paragraph (e)(2), the second sentence is amended by revising the words "method 21 of part 60, appendix A" to read "Method 21 of Appendix A to 40 CFR Part 60."

c. In paragraph (e)(2)(ii)(B), fourth sentence, the words "method 21" are revised to read "Method 21 of Appendix A to 40 CFR Part 60."

d. In paragraph (h), the first sentence is amended by revising the words "method 27 of part 60, appendix A" to read "Method 27 of Appendix A to 40 CFR Part 60."

**§ 61.303 [Amended]**

52. In § 61.303, paragraphs (c), (c)(1), and (c)(2) are amended by revising the words "44 MW" to read "44 MW (150 × 10<sup>6</sup> BTU/hr)" wherever they occur.

**§ 61.304 [Amended]**

53. Amend § 61.304 as follows:

a. Paragraph (a)(4)(iii) is amended by revising the word "method" to read "Method."

b. In paragraph (a)(4)(iv), the first sentence is amended by revising the words "method 25A or method 25B" to read "Method 25A or Method 25B."

c. Paragraph (b) is amended by revising the words "a performance test according to method 22 of appendix A of this part, shall be performed to determine visible emissions. The observation period shall be at least 2 hours and shall be conducted according to method 22" to read "a performance test according to Method 22 of appendix A of 40 CFR part 60 shall be performed to determine visible emissions. The observation period shall be at least 2 hours."

54. Amend § 61.305 as follows:

a. Paragraphs (a), (b)(3), and (d) are amended by revising the words "44 MW" to read "44 MW (150 × 10<sup>6</sup> BTU/hr)" wherever they occur.

b. Paragraph (a)(3)(ii) is revised.

c. Paragraphs (b)(1), (b)(2), and (b)(3) are amended by revising the words "28 °C" to read "28 °C (50 °F)" wherever they occur.

The revisions read as follows:

**§ 61.305 Reporting and recordkeeping.**

(a) \* \* \*

(3) \* \* \*

(ii) The average combustion temperature of the steam generating unit or process heater with a design heat input capacity of less than 44 MW (150 × 10<sup>6</sup> BTU/hr), measured with the following frequency: at least every 2 minutes during a loading cycle if the total time period of the loading cycle is less than 3 hours, and every 15 minutes if the total time period of the loading cycle is equal to or greater than 3 hours. The measured temperature shall be averaged over the loading cycle.

\* \* \* \* \*

**§ 61.342 [Amended]**

55. Amend § 61.342 as follows:

a. In paragraph (a), the first sentence, the words "10 megagrams per year (Mg/yr)" are revised to read "10 megagrams per year (Mg/yr) (11 ton/yr)."

b. Paragraphs (a)(3), (b), (c), (c)(3)(i), (d), and (e) are amended by revising the words "10 Mg/yr" to read "10 Mg/yr (11 ton/yr)."

c. Paragraph (c)(3)(i) is amended by revising the words "0.02 liters per minute" to read "0.02 liters per minute (0.005 gallons per minute)."

d. Paragraph (c)(3)(ii)(B) is amended by revising the words "2.0 Mg/yr" to read "2.0 Mg/yr (2.2 ton/yr)."

e. Paragraph (d)(2)(1) is redesignated as paragraph (d)(2)(i).

f. In paragraph (d)(2)(i), the first sentence is amended by revising the words "1 Mg/yr" to read "1 Mg/yr (1.1 ton/yr)."

g. In paragraph (e)(2)(i), the first sentence is amended by revising the words "6.0 Mg/yr" to read "6.0 Mg/yr (6.6 ton/yr)."

#### § 61.348 [Amended]

56. Amend § 61.348 as follows:

a. In paragraph (b)(2)(ii), the first sentence is amended by revising the words "1 Mg/yr" to read "1 Mg/yr (1.1 ton/yr)."

b. In paragraph (b)(2)(ii)(B), by revising the third sentence.

The revision reads as follows:

#### § 61.348 Standards: Treatment processes.

(b) \* \* \*

(2) \* \* \*

(ii) \* \* \*

(B) \* \* \* An enhanced biodegradation unit typically operates at a food-to-microorganism ratio in the range of 0.05 to 1.0 kg of biological oxygen demand per kg of biomass per day, a mixed liquor suspended solids ratio in the range of 1 to 8 grams per liter (0.008 to 0.7 pounds per liter), and a residence time in the range of 3 to 36 hours.

\* \* \* \* \*

#### § 61.349 [Amended]

57. In § 61.349, paragraph (a)(2)(i)(C) is amended by revising the words "760 °C" to read "760 °C (1,400 °F)."

#### § 61.354 [Amended]

58. In § 61.354, paragraph (c)(4) is amended by revising the words "44 megawatts (MW)" to read "44 MW (150 × 10<sup>6</sup> BTU/hr)."

58a. In paragraph (c)(5), "44 MW" is revised to read "44 MW (150 × 10<sup>6</sup> BTU/hr)."

#### § 61.355 [Amended]

59. Amend § 61.355 as follows:

a. Paragraphs (a)(3), (a)(4), (a)(4)(ii) are amended by revising the words "10 Mg/yr" to read "10 Mg/yr (11 ton/yr)" wherever they occur.

b. Paragraphs (a)(4), (a)(5), and (a)(5)(ii) are amended by revising the words "1 Mg/yr" to read "1 Mg/yr (1.1 ton/yr)" wherever they occur.

c. Paragraphs (c)(3)(ii)(F) and (c)(3)(ii)(H) are amended by revising the words "10 °C" to read "10 °C (50 °F)" wherever they occur.

d. Paragraph (c)(3)(v) is amended by revising the words "kg/yr" to read "kg/yr (lb/yr)" wherever they occur.

e. Paragraphs (e)(3), (e)(4), (f)(3), (f)(4)(iv), (f)(5), (i)(3)(iv), and (i)(4) are

amended by revising the definitions of the terms used in the equations; and (f)(4)(iii) and (i)(3)(iii) are amended by revising the equation and definitions of terms used in the equations.

f. Paragraphs (f)(4)(ii)(B), (f)(4)(ii)(C), (h)(1), (h)(2), (h)(3), (h)(5), (h)(6), (i)(2), (i)(3)(ii)(B), and (i)(3)(ii)(C) are amended by revising the word "method" to read "Method" wherever it occurs.

g. Paragraph (k)(7) is amended by revising the words "6.0 Mg/yr" to read "6.0 Mg/yr (6.6 ton/yr)."

The revisions read as follows:

#### § 61.355 Test methods, procedures, and compliance provisions.

\* \* \* \* \*

(e) \* \* \*

(3) \* \* \*

E<sub>b</sub> = Mass flow rate of benzene entering the treatment process, kg/hr (lb/hr).

K = Density of the waste stream, kg/m<sup>3</sup> (lb/ft<sup>3</sup>).

V<sub>i</sub> = Average volume flow rate of waste entering the treatment process during each run i, m<sup>3</sup>/hr (ft<sup>3</sup>/hr).

C<sub>i</sub> = Average concentration of benzene in the waste stream entering the treatment process during each run i, ppmw.

n = Number of runs.

10<sup>6</sup> = Conversion factor for ppmw.

(4) \* \* \*

E<sub>a</sub> = Mass flow rate of benzene exiting the treatment process, kg/hr (lb/hr).

K = Density of the waste stream, kg/m<sup>3</sup> (lb/ft<sup>3</sup>).

V<sub>i</sub> = Average volume flow rate of waste exiting the treatment process during each run i, m<sup>3</sup>/hr (ft<sup>3</sup>/hr).

C<sub>i</sub> = Average concentration of benzene in the waste stream exiting the treatment process during each run i, ppmw.

n = Number of runs.

10<sup>6</sup> = Conversion factor for ppmw.

(f) \* \* \*

(3) \* \* \*

E<sub>b</sub> = Mass flow rate of benzene entering the combustion unit, kg/hr (lb/hr).

K = Density of the waste stream, kg/m<sup>3</sup> (lb/ft<sup>3</sup>).

V<sub>i</sub> = Average volume flow rate of waste entering the combustion unit during each run i, m<sup>3</sup>/hr (ft<sup>3</sup>/hr).

C<sub>i</sub> = Average concentration of benzene in the waste stream entering the combustion unit during each run i, ppmw.

n = Number of runs.

10<sup>6</sup> = Conversion factor for ppmw.

(4) \* \* \*

(iii) \* \* \*

$$M_i = D_b VC(10^{-6})$$

Where:

M<sub>i</sub> = Mass of benzene emitted during run i, kg (lb).

V = Volume of air-vapor mixture exhausted at standard conditions, m<sup>3</sup> (ft<sup>3</sup>).

C = Concentration of benzene measured in the exhaust, ppmv.

D<sub>b</sub> = Density of benzene, 3.24 kg/m<sup>3</sup> (0.202 lb/ft<sup>3</sup>).

10<sup>6</sup> = Conversion factor for ppmv.

(iv) \* \* \*

E<sub>a</sub> = Mass flow rate of benzene emitted from the combustion unit, kg/hr (lb/hr).

M<sub>i</sub> = Mass of benzene emitted from the combustion unit during run i, kg (lb).

T = Total time of all runs, hr.

n = Number of runs.

(5) \* \* \*

R = Benzene destruction efficiency for the combustion unit, percent.

E<sub>b</sub> = Mass flow rate of benzene entering the combustion unit, kg/hr (lb/hr).

E<sub>a</sub> = Mass flow rate of benzene emitted from the combustion unit, kg/hr (lb/hr).

\* \* \* \* \*

(i) \* \* \*

(3) \* \* \*

(iii) \* \* \*

$$M_{aj} = \frac{K_l V_{aj}}{10^6} \left( \sum_{i=1}^n C_{ai} MW_i \right)$$

$$M_{bj} = \frac{K_l V_{bj}}{10^6} \left( \sum_{i=1}^n C_{bi} MW_i \right)$$

M<sub>aj</sub> = Mass of organics or benzene in the vent stream entering the control device during run j, kg (lb).

M<sub>bj</sub> = Mass of organics or benzene in the vent stream exiting the control device during run j, kg (lb).

V<sub>aj</sub> = Volume of vent stream entering the control device during run j, at standard conditions, m<sup>3</sup> (ft<sup>3</sup>).

V<sub>bj</sub> = Volume of vent stream exiting the control device during run j, at standard conditions, m<sup>3</sup> (ft<sup>3</sup>).

C<sub>ai</sub> = Organic concentration of compound i or the benzene concentration measured in the vent stream entering the control device as determined by Method 18, ppm by volume on a dry basis.

C<sub>bi</sub> = Organic concentration of compound i or the benzene concentration measured in the vent stream exiting the control device as determined by Method 18, ppm by volume on a dry basis.

MW<sub>i</sub> = Molecular weight of organic compound i in the vent stream, or the molecular weight of benzene, kg/kg-mol (lb/lb-mole).

n = Number of organic compounds in the vent stream; if benzene reduction efficiency is being demonstrated, then n=1.

$K_1$  = Conversion factor for molar volume at standard conditions (293 K and 760 mm Hg (527 R and 14.7 psia)) = 0.0416 kg-mol/m<sup>3</sup> (0.00118 lb-mol/ft<sup>3</sup>)

$10^{-6}$  = Conversion factor for ppmv.

(iv) \* \* \*

$E_a$  = Mass flow rate of organics or benzene entering the control device, kg/hr (lb/hr).

$E_b$  = Mass flow rate of organics or benzene exiting the control device, kg/hr (lb/hr).

$M_{aj}$  = Mass of organics or benzene in the vent stream entering the control device during run j, kg (lb).

$M_{bj}$  = Mass of organics or benzene in the vent stream exiting the control device during run j, kg (lb).

T = Total time of all runs, hr.

n = Number of runs.

(4) \* \* \*

R = Total organic reduction of efficiency or benzene reduction efficiency for the control device, percent.

$E_b$  = Mass flow rate of organics or benzene entering the control device, kg/hr (lb/hr).

$E_a$  = Mass flow rate of organic or benzene emitted from the control device, kg/hr (lb/hr).

\* \* \* \*

**§ 61.356 [Amended]**

60. Amend § 61.356 as follows:

a. Paragraph (b)(2)(i) is amended by revising the words "0.02 liters per minute" to read "0.02 liters (0.005 gallons) per minute."

b. Paragraph (b)(2)(i) is amended by revising the words "10 Mg/yr" to read "10 Mg/yr (11 ton/yr)."

c. Paragraph (b)(2)(ii) is amended by revising the words "2.0 Mg/yr" to read "2.0 Mg/yr (2.2 ton/yr)."

d. Paragraph (b)(4) is amended by revising the words "6.0 Mg/yr" to read "6.0 Mg/yr (6.6 ton/yr)."

e. Paragraphs (j)(4), (j)(5), and (j)(6) are amended by revising the words "28 °C" to read "28 °C (50 °F)" wherever they occur.

f. Paragraph (j)(6) is amended by revising the words "44 MW" to read "44 MW (150 × 106 BTU/hr)" wherever they occur.

g. Paragraph (j)(8) is amended by revising the words "6 °C" to read "6 °C (11 °F)" wherever they occur.

**§ 61.357 [Amended]**

61. Amend § 61.357 as follows:

a. Paragraphs (b) and (c) are amended by revising the words "1 Mg/yr" to read "1 Mg/yr (1.1 ton/yr)" wherever they occur.

b. Paragraphs (c) and (d) are amended by revising the words "10 Mg/yr" to read "10 Mg/yr (11 ton/yr)" wherever they occur.

c. Paragraphs (d)(7)(iv)(A), (d)(7)(iv)(B), and (d)(7)(iv)(C) are amended by revising the words "28 °C" to read "28 °C (50 °F)" wherever they occur.

d. Paragraph (d)(7)(iv)(C) is amended by revising the words "44 MW" to read "44 MW (150 × 106 BTU/hr)."

e. Paragraph (d)(7)(iv)(E) is amended by revising the words "6 °C" to read "6 °C (11 °F)."

62. In Part 61, Appendix B is amended by revising Methods 101, 101A, 102, 103, 104, 105, 106, 107, 107A, 108, 108A, 108B, 108C, and 111 to read as follows:

**Method 101—Determination of Particulate and Gaseous Mercury Emissions From Chlor-Alkali Plants (Air Streams)**

**Note:** This method does not include all of the specifications (e.g., equipment and supplies) and procedures (e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from methods in Appendix A to 40 CFR Part 60. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, and Method 5.

**1.0 Scope and Application**

**1.1 Analytes.**

Analyte	CAS No.	Sensitivity
Mercury (Hg) .....	7439–97–6	Dependent upon recorder and spectrophotometer.

**1.2 Applicability.** This method is applicable for the determination of Hg emissions, including both particulate and gaseous Hg, from chlor-alkali plants and other sources (as specified in the regulations) where the carrier-gas stream in the duct or stack is principally air.

**1.3 Data Quality Objectives.** Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

**2.0 Summary of Method**

Particulate and gaseous Hg emissions are withdrawn isokinetically from the source and collected in acidic iodine monochloride (ICl) solution. The Hg collected (in the mercuric form) is reduced to elemental Hg, which is then aerated from the solution into an optical cell and measured by atomic absorption spectrophotometry.

**3.0 Definitions [Reserved]**

**4.0 Interferences**

**4.1 Sample Collection.** Sulfur dioxide (SO<sub>2</sub>) reduces ICl and causes premature depletion of the ICl solution.

**4.2 Sample Analysis.**

**4.2.1** ICl concentrations greater than 10<sup>-4</sup> molar inhibit the reduction of the Hg (II) ion in the aeration cell.

**4.2.2** Condensation of water vapor on the optical cell windows causes a positive interference.

**5.0 Safety**

**5.1 Disclaimer.** This method may involve hazardous materials, operations, and equipment. This test method does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

**5.2 Corrosive Reagents.** The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burn as thermal burn.

**5.2.1 Hydrochloric Acid (HCl).** Highly toxic and corrosive. Causes severe damage to tissues. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or edema of lungs. Exposure to concentrations of 0.13 to 0.2 percent can be lethal to humans in a few minutes. Provide ventilation to limit exposure. Reacts with metals, producing hydrogen gas.

**5.2.2 Nitric Acid (HNO<sub>3</sub>).** Highly corrosive to eyes, skin, nose, and lungs. Vapors cause bronchitis, pneumonia, or edema of lungs. Reaction to inhalation may be delayed as long as 30 hours and

still be fatal. Provide ventilation to limit exposure. Strong oxidizer. Hazardous reaction may occur with organic materials such as solvents.

5.2.3 Sulfuric Acid ( $\text{H}_2\text{SO}_4$ ). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes.  $3 \text{ mg/m}^3$  will cause lung damage.  $1 \text{ mg/m}^3$  for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

#### 6.0 Equipment and Supplies.

6.1 Sample Collection. A schematic of the sampling train used in performing this method is shown in Figure 101-1; it is similar to the Method 5 sampling train. The following items are required for sample collection:

6.1.1 Probe Nozzle, Pitot Tube, Differential Pressure Gauge, Metering System, Barometer, and Gas Density Determination Equipment. Same as Method 5, Sections 6.1.1.1, 6.1.1.3, 6.1.1.4, 6.1.1.9, 6.1.2, and 6.1.3, respectively.

6.1.2 Probe Liner. Borosilicate or quartz glass tubing. A heating system capable of maintaining a gas temperature of  $120 \pm 14^\circ\text{C}$  ( $248 \pm 25^\circ\text{F}$ ) at the probe exit during sampling may be used to prevent water condensation.

**Note:** Do not use metal probe liners.

6.1.3 Impingers. Four Greenburg-Smith impingers connected in series with leak-free ground glass fittings or any similar leak-free noncontaminating fittings. For the first, third, and fourth impingers, impingers that are modified by replacing the tip with a 13-mm ID (0.5-in.) glass tube extending to 13 mm (0.5 in.) from the bottom of the flask may be used.

6.1.4 Acid Trap. Mine Safety Appliances air line filter, Catalog number 81857, with acid absorbing cartridge and suitable connections, or equivalent.

6.2 Sample Recovery. The following items are needed for sample recovery:

6.2.1 Glass Sample Bottles. Leakless, with Teflon-lined caps, 1000- and 100-ml.

6.2.2 Graduated Cylinder. 250-ml.

6.2.3 Funnel and Rubber Policeman. To aid in transfer of silica gel to container; not necessary if silica gel is weighed in the field.

6.2.4 Funnel. Glass, to aid in sample recovery.

6.3 Sample Preparation and Analysis. The following items are needed for sample preparation and analysis:

6.3.1 Atomic Absorption Spectrophotometer. Perkin-Elmer 303, or equivalent, containing a hollow-cathode mercury lamp and the optical cell described in Section 6.3.2.

6.3.2 Optical Cell. Cylindrical shape with quartz end windows and having the dimensions shown in Figure 101-2. Wind the cell with approximately 2 meters (6 ft) of 24-gauge Nichrome wire, or equivalent, and wrap with fiberglass insulation tape, or equivalent; do not let the wires touch each other.

6.3.3 Aeration Cell. Constructed according to the specifications in Figure 101-3. Do not use a glass frit as a substitute for the blown glass bubbler tip shown in Figure 101-3.

6.3.4 Recorder. Matched to output of the spectrophotometer described in Section 6.3.1.

6.3.5 Variable Transformer. To vary the voltage on the optical cell from 0 to 40 volts.

6.3.6 Hood. For venting optical cell exhaust.

6.3.7 Flow Metering Valve.

6.3.8 Rate Meter. Rotameter, or equivalent, capable of measuring to within 2 percent a gas flow of 1.5 liters/min ( $0.053 \text{ cfm}$ ).

6.3.9 Aeration Gas Cylinder. Nitrogen or dry, Hg-free air, equipped with a single-stage regulator.

6.3.10 Tubing. For making connections. Use glass tubing (ungreased ball and socket connections are recommended) for all tubing connections between the solution cell and the optical cell; do not use Tygon tubing, other types of flexible tubing, or metal tubing as substitutes. Teflon, steel, or copper tubing may be used between the nitrogen tank and flow metering valve (Section 6.3.7), and Tygon, gum, or rubber tubing between the flow metering valve and the aeration cell.

6.3.11 Flow Rate Calibration Equipment. Bubble flow meter or wet-test meter for measuring a gas flow rate of  $1.5 \pm 0.1 \text{ liters/min}$  ( $0.053 \pm 0.0035 \text{ cfm}$ ).

6.3.12 Volumetric Flasks. Class A with penny head standard taper stoppers; 100-, 250-, 500-, and 1000-ml.

6.3.13 Volumetric Pipets. Class A; 1-, 2-, 3-, 4-, and 5-ml.

6.3.14 Graduated Cylinder. 50-ml.

6.3.15 Magnetic Stirrer. General-purpose laboratory type.

6.3.16 Magnetic Stirring Bar. Teflon-coated.

6.3.17 Balance. Capable of weighing to  $\pm 0.5 \text{ g}$ .

6.3.18 Alternative Analytical Apparatus. Alternative systems are allowable as long as they meet the following criteria:

6.3.18.1 A linear calibration curve is generated and two consecutive samples of the same aliquot size and concentration agree within 3 percent of their average.

6.3.18.2 A minimum of 95 percent of the spike is recovered when an aliquot of a source sample is spiked with a known concentration of Hg (II) compound.

6.3.18.3 The reducing agent should be added after the aeration cell is closed.

6.3.18.4 The aeration bottle bubbler should not contain a frit.

6.3.18.5 Any Tygon tubing used should be as short as possible and conditioned prior to use until blanks and standards yield linear and reproducible results.

6.3.18.6 If manual stirring is done before aeration, it should be done with the aeration cell closed.

6.3.18.7 A drying tube should not be used unless it is conditioned as the Tygon tubing above.

#### 7.0 Reagents and Standards

Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society; where such specifications are not available, use the best available grade.

7.1 Sample Collection. The following reagents are required for sample collection:

7.1.1 Water. Deionized distilled, to conform to ASTM D 1193-77 or 91 (incorporated by reference—see § 61.18), Type 1. If high concentrations of organic matter are not expected to be present, the analyst may eliminate the  $\text{KMnO}_4$  test for oxidizable organic matter. Use this water in all dilutions and solution preparations.

7.1.2 Nitric Acid, 50 Percent (v/v). Mix equal volumes of concentrated  $\text{HNO}_3$  and water, being careful to add the acid to the water slowly.

7.1.3 Silica Gel. Indicating type, 6- to 16-mesh. If previously used, dry at  $175^\circ\text{C}$  ( $350^\circ\text{F}$ ) for 2 hours. The tester may use new silica gel as received.

7.1.4 Potassium Iodide (KI) Solution, 25 Percent. Dissolve 250 g of KI in water, and dilute to 1 liter.

7.1.5 Iodine Monochloride Stock Solution, 1.0 M. To 800 ml of 25 percent KI solution, add 800 ml of concentrated  $\text{HCl}$ . Cool to room temperature. With vigorous stirring, slowly add 135 g of potassium iodate ( $\text{KIO}_3$ ), and stir until all free iodine has dissolved. A clear orange-red solution occurs when all the  $\text{KIO}_3$  has been added. Cool to room temperature, and dilute to 1800 ml with

water. Keep the solution in amber glass bottles to prevent degradation.

7.1.6 Absorbing Solution, 0.1 M ICl. Dilute 100 ml of the 1.0 M ICl stock solution to 1 liter with water. Keep the solution in amber glass bottles and in darkness to prevent degradation. This reagent is stable for at least two months.

7.2 Sample Preparation and Analysis. The following reagents and standards are required for sample preparation and analysis:

7.2.1 Reagents.

7.2.1.1 Tin (II) Solution. Prepare fresh daily, and keep sealed when not being used. Completely dissolve 20 g of tin (II) chloride (or 25 g of tin (II) sulfate) crystals (Baker Analyzed reagent grade or any other brand that will give a clear solution) in 25 ml of concentrated HCl. Dilute to 250 ml with water. Do not substitute  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ , or other strong acids for the HCl.

7.2.1.2 Sulfuric Acid, 5 Percent (v/v). Dilute 25 ml of concentrated  $\text{H}_2\text{SO}_4$  to 500 ml with water.

7.2.2 Standards

7.2.2.1 Hg Stock Solution, 1 mg Hg/ml. Prepare and store all Hg standard solutions in borosilicate glass containers. Completely dissolve 0.1354 g of Hg (II) chloride in 75 ml of water in a 100-ml glass volumetric flask. Add 10 ml of concentrated  $\text{HNO}_3$ , and adjust the volume to exactly 100 ml with water. Mix thoroughly. This solution is stable for at least one month.

7.2.2.2 Intermediate Hg Standard Solution, 10  $\mu\text{g}$  Hg/ml. Prepare fresh weekly. Pipet 5.0 ml of the Hg stock solution (Section 7.2.2.1) into a 500-ml glass volumetric flask, and add 20 ml of the 5 percent  $\text{H}_2\text{SO}_4$  solution. Dilute to exactly 500 ml with water. Thoroughly mix the solution.

7.2.2.3 Working Hg Standard Solution, 200 ng Hg/ml. Prepare fresh daily. Pipet 5.0 ml of the intermediate Hg standard solution (Section 7.2.2.2) into a 250-ml volumetric glass flask. Add 10 ml of the 5 percent  $\text{H}_2\text{SO}_4$  and 2 ml of the 0.1 M ICl absorbing solution taken as a blank (Section 8.7.4.3), and dilute to 250 ml with water. Mix thoroughly.

8.0 Sample Collection, Preservation, Transport, and Storage

Because of the complexity of this method, testers should be trained and experienced with the test procedures to ensure reliable results. Since the amount of Hg that is collected generally is small, the method must be carefully applied to prevent contamination or loss of sample.

8.1 Pretest Preparation. Follow the general procedure outlined in Method 5,

Section 8.1, except omit Sections 8.1.2 and 8.1.3.

8.2 Preliminary Determinations. Follow the general procedure outlined in Method 5, Section 8.2, with the exception of the following:

8.2.1 Select a nozzle size based on the range of velocity heads to assure that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates below 28 liters/min (1.0 cfm).

8.2.2 Perform test runs such that samples are obtained over a period or periods that accurately determine the maximum emissions that occur in a 24-hour period. In the case of cyclic operations, run sufficient tests for the accurate determination of the emissions that occur over the duration of the cycle. A minimum sample time of 2 hours is recommended. In some instances, high Hg or high  $\text{SO}_2$  concentrations make it impossible to sample for the desired minimum time. This is indicated by reddening (liberation of free iodine) in the first impinger. In these cases, the sample run may be divided into two or more subruns to ensure that the absorbing solution is not depleted.

8.3 Preparation of Sampling Train.

8.3.1 Clean all glassware (probe, impingers, and connectors) by rinsing with 50 percent  $\text{HNO}_3$ , tap water, 0.1 M ICl, tap water, and finally deionized distilled water. Place 100 ml of 0.1 M ICl in each of the first three impingers. Take care to prevent the absorbing solution from contacting any greased surfaces. Place approximately 200 g of preweighed silica gel in the fourth impinger. More silica gel may be used, but care should be taken to ensure that it is not entrained and carried out from the impinger during sampling. Place the silica gel container in a clean place for later use in the sample recovery. Alternatively, determine and record the weight of the silica gel plus impinger to the nearest 0.5 g.

8.3.2 Install the selected nozzle using a Viton A O-ring when stack temperatures are less than 260 °C (500 °F). Use a fiberglass string gasket if temperatures are higher. See APTD-0576 (Reference 3 in Method 5) for details. Other connecting systems using either 316 stainless steel or Teflon ferrules may be used. Mark the probe with heat-resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

8.3.3 Assemble the train as shown in Figure 101-1, using (if necessary) a very light coat of silicone grease on all ground glass joints. Grease only the outer portion (see APTD-0576) to avoid

the possibility of contamination by the silicone grease.

**Note:** An empty impinger may be inserted between the third impinger and the silica gel to remove excess moisture from the sample stream.

8.3.4 After the sampling train has been assembled, turn on and set the probe heating system, if applicable, at the desired operating temperature. Allow time for the temperatures to stabilize. Place crushed ice around the impingers.

8.4 Leak-Check Procedures. Follow the leak-check procedures outlined in Method 5, Section 8.4.

8.5 Sampling Train Operation. Follow the general procedure outlined in Method 5, Section 8.5. For each run, record the data required on a data sheet such as the one shown in Figure 101-4.

8.6 Calculation of Percent Isokinetic. Same as Method 5, Section 8.6.

8.7 Sample Recovery. Begin proper cleanup procedure as soon as the probe is removed from the stack at the end of the sampling period.

8.7.1 Allow the probe to cool. When it can be safely handled, wipe off any external particulate matter near the tip of the probe nozzle, and place a cap over it. Do not cap off the probe tip tightly while the sampling train is cooling. Capping would create a vacuum and draw liquid out from the impingers.

8.7.2 Before moving the sampling train to the cleanup site, remove the probe from the train, wipe off the silicone grease, and cap the open outlet of the probe. Be careful not to lose any condensate that might be present. Wipe off the silicone grease from the impinger. Use either ground-glass stoppers, plastic caps, or serum caps to close these openings.

8.7.3 Transfer the probe and impinger assembly to a cleanup area that is clean, protected from the wind, and free of Hg contamination. The ambient air in laboratories located in the immediate vicinity of Hg-using facilities is not normally free of Hg contamination.

8.7.4 Inspect the train before and during disassembly, and note any abnormal conditions. Treat the samples as follows.

8.7.4.1 Container No. 1 (Impingers and Probe).

8.7.4.1.1 Using a graduated cylinder, measure the liquid in the first three impingers to within 1 ml. Record the volume of liquid present (e.g., see Figure 5-6 of Method 5). This information is needed to calculate the moisture content of the effluent gas.

(Use only glass storage bottles and graduated cylinders that have been precleaned as in Section 8.3.1) Place the contents of the first three impingers into a 1000-ml glass sample bottle.

8.7.4.1.2 Taking care that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover the Hg (and any condensate) from the probe nozzle, probe fitting, and probe liner as follows: Rinse these components with two 50-ml portions of 0.1 M ICl. Next, rinse the probe nozzle, fitting and liner, and each

piece of connecting glassware between the probe liner and the back half of the third impinger with a maximum of 400 ml of water. Add all washings to the 1000-ml glass sample bottle containing the liquid from the first three impingers.

8.7.4.1.3 After all washings have been collected in the sample container, tighten the lid on the container to prevent leakage during shipment to the laboratory. Mark the height of the liquid to determine later whether leakage occurred during transport. Label the container to identify clearly its contents.

8.7.4.2 Container No. 2 (Silica Gel). Same as Method 5, Section 8.7.6.3.

8.7.4.3 Container No. 3 (Absorbing Solution Blank). Place 50 ml of the 0.1 M ICl absorbing solution in a 100-ml sample bottle. Seal the container. Use this blank to prepare the working Hg standard solution (Section 7.2.2.3).

## 9.0 Quality Control

### 9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.4 10.2 .....	Sampling equipment leak-checks and calibration .....	Ensure accuracy and precision of sampling measurements.
10.5, 10.6 .....	Spectrophotometer calibration .....	Ensure linearity of spectrophotometer response to standards.
11.3.3 .....	Check for matrix effects .....	Eliminate matrix effects.

9.2 Volume Metering System Checks. Same as Method 5, Section 9.2.

## 10.0 Calibration and Standardizations

**Note:** Maintain a laboratory log of all calibrations.

10.1 Before use, clean all glassware, both new and used, as follows: brush with soap and tap water, liberally rinse with tap water, soak for 1 hour in 50 percent HNO<sub>3</sub>, and then rinse with deionized distilled water.

10.2 Sampling Equipment. Calibrate the sampling equipment according to the procedures outlined in the following sections of Method 5: Section 10.1 (Probe Nozzle), Section 10.2 (Pitot Tube Assembly), Section 10.3 (Metering System), Section 10.5 (Temperature Sensors), Section 10.6 (Barometer).

10.3 Aeration System Flow Rate Meter. Assemble the aeration system as shown in Figure 101–5. Set the outlet pressure on the aeration gas cylinder regulator to a minimum pressure of 500 mm Hg (10 psi), and use the flow metering valve and a bubble flowmeter or wet-test meter to obtain a flow rate of  $1.5 \pm 0.1$  liters/min ( $0.053 \pm 0.0035$  cfm) through the aeration cell. After the calibration of the aeration system flow rate meter is complete, remove the bubble flowmeter from the system.

10.4 Optical Cell Heating System. Using a 50-ml graduated cylinder, add 50 ml of water to the bottle section of the aeration cell, and attach the bottle section to the bubbler section of the cell. Attach the aeration cell to the optical cell and while aerating at  $1.5 \pm 0.1$  liters/min ( $0.053 \pm 0.0035$  cfm), determine the minimum variable transformer setting necessary to prevent condensation of moisture in the optical cell and in the connecting tubing. (This setting should not exceed 20 volts.)

10.5 Spectrophotometer and Recorder.

10.5.1 The Hg response may be measured by either peak height or peak area.

**Note:** The temperature of the solution affects the rate at which elemental Hg is released from a solution and, consequently, it affects the shape of the absorption curve (area) and the point of maximum absorbance (peak height). Therefore, to obtain reproducible results, bring all solutions to room temperature before use.

10.5.2 Set the spectrophotometer wavelength at 253.7 nm, and make certain the optical cell is at the minimum temperature that will prevent water condensation. Then set the recorder scale as follows: Using a 50-ml graduated cylinder, add 50 ml of water to the aeration cell bottle. Add three drops of Antifoam B to the bottle, and then pipet 5.0 ml of the working Hg standard solution into the aeration cell.

**Note:** Always add the Hg-containing solution to the aeration cell after the 50 ml of water.

10.5.3 Place a Teflon-coated stirring bar in the bottle. Before attaching the bottle section to the bubbler section of the aeration cell, make certain that (1) the aeration cell exit arm stopcock (Figure 101–3) is closed (so that Hg will not prematurely enter the optical cell when the reducing agent is being added) and (2) there is no flow through the bubbler. If conditions (1) and (2) are met, attach the bottle section to the bubbler section of the aeration cell. Pipet 5 ml of tin (II) reducing solution into the aeration cell through the side arm, and immediately stopper the side arm. Stir the solution for 15 seconds, turn on the recorder, open the aeration cell exit arm stopcock, and immediately initiate aeration with continued stirring. Determine the maximum absorbance of

the standard, and set this value to read 90 percent of the recorder full scale.

### 10.6 Calibration Curve.

10.6.1 After setting the recorder scale, repeat the procedure in Section 10.5 using 0.0-, 1.0-, 2.0-, 3.0-, 4.0-, and 5.0-ml aliquots of the working standard solution (final amount of Hg in the aeration cell is 0, 200, 400, 600, 800, and 1000 ng, respectively). Repeat this procedure on each aliquot size until two consecutive peaks agree within 3 percent of their average value.

**Note:** To prevent Hg carryover from one sample to another, do not close the aeration cell from the optical cell until the recorder pen has returned to the baseline.)

10.6.2 It should not be necessary to disconnect the aeration gas inlet line from the aeration cell when changing samples. After separating the bottle and bubbler sections of the aeration cell, place the bubbler section into a 600-ml beaker containing approximately 400 ml of water. Rinse the bottle section of the aeration cell with a stream of water to remove all traces of the tin (II) reducing agent. Also, to prevent the loss of Hg before aeration, remove all traces of the reducing agent between samples by washing with water. It will be necessary, however, to wash the aeration cell parts with concentrated HCl if any of the following conditions occur: (1) A white film appears on any inside surface of the aeration cell, (2) the calibration curve changes suddenly, or (3) the replicate samples do not yield reproducible results.

10.6.3 Subtract the average peak height (or peak area) of the blank (0.0-ml aliquot)—which must be less than 2 percent of recorder full scale—from the averaged peak heights of the 1.0-, 2.0-, 3.0-, 4.0-, and 5.0-ml aliquot standards. If the blank absorbance is greater than 2 percent of full-scale, the probable

cause is Hg contamination of a reagent or carry-over of Hg from a previous sample. Prepare the calibration curve by plotting the corrected peak height of each standard solution versus the corresponding final total Hg weight in the aeration cell (in ng), and draw the best fit straight line. This line should either pass through the origin or pass through a point no further from the origin than  $\pm 2$  percent of the recorder full scale. If the line does not pass through or very near to the origin, check for nonlinearity of the curve and for incorrectly prepared standards.

#### 11.0 Analytical Procedure

11.1 Sample Loss Check. Check the liquid level in each container to see whether liquid was lost during transport. If a noticeable amount of leakage occurred, either void the sample or use methods subject to the approval of the Administrator to account for the losses.

11.2 Sample Preparation. Treat each sample as follows:

11.2.1 Container No. 1 (Impingers and Probe). Carefully transfer the contents of Container No. 1 into a 1000-ml volumetric flask, and adjust the volume to exactly 1000 ml with water.

11.2.2 Dilutions. Pipet a 2-ml aliquot from the diluted sample from Section 11.2.1 into a 250-ml volumetric flask. Add 10 ml of 5 percent  $H_2SO_4$ , and adjust the volume to exactly 250 ml with water. This solution is stable for at least 72 hours.

**Note:** The dilution factor will be 250/2 for this solution.

11.3 Analysis. Calibrate the analytical equipment and develop a calibration curve as outlined in Sections 10.3 through 10.6.

11.3.1 Mercury Samples. Repeat the procedure used to establish the calibration curve with an appropriately sized aliquot (1 to 5 ml) of the diluted sample (from Section 11.2.2) until two consecutive peak heights agree within 3 percent of their average value. The peak maximum of an aliquot (except the 5-ml aliquot) must be greater than 10 percent of the recorder full scale. If the peak maximum of a 1.0-ml aliquot is off scale on the recorder, further dilute the original source sample to bring the Hg concentration into the calibration range of the spectrophotometer.

11.3.2 Run a blank and standard at least after every five samples to check the spectrophotometer calibration. The peak height of the blank must pass through a point no further from the origin than  $\pm 2$  percent of the recorder full scale. The difference between the measured concentration of the standard (the product of the corrected peak height and the reciprocal of the least squares slope) and the actual concentration of the standard must be less than 7 percent, or recalibration of the analyzer is required.

11.3.3 Check for Matrix Effects (optional). Use the Method of Standard Additions as follows to check at least one sample from each source for matrix effects on the Hg results. The Method of Standard Additions procedures described on pages 9-4 and 9-5 of the section entitled "General Information" of the Perkin Elmer Corporation Atomic Absorption Spectrophotometry Manual, Number 303-0152 (Reference 16 in Section 16.0) are recommended. If the results of the Method of Standard Additions procedure used on the single source sample do not agree to within  $\pm 5$  percent of the value obtained by the routine atomic absorption analysis, then

reanalyze all samples from the source using the Method of Standard Additions procedure.

11.4 Container No. 2 (Silica Gel). Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance. (This step may be conducted in the field.)

#### 12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra decimal significant figure beyond that of the acquired data. Round off figures only after the final calculation. Other forms of the equations may be used as long as they give equivalent results.

12.1 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop, Dry Gas Volume, Volume of Water Vapor Condensed, Moisture Content, and Isokinetic Variation. Same as Method 5, Sections 12.2 through 12.5 and 12.11, respectively.

12.2 Stack Gas Velocity. Using the data from this test and Equation 2-9 of Method 2, calculate the average stack gas velocity  $v_s$ .

12.3 Total Mercury.

12.3.1 For each source sample, correct the average maximum absorbance of the two consecutive samples whose peak heights agree within 3 percent of their average for the contribution of the solution blank (see Section 10.6.3). Use the calibration curve and these corrected averages to determine the final total weight of Hg in ng in the aeration cell for each source sample.

12.3.2 Correct for any dilutions made to bring the sample into the working range of the spectrophotometer. Then calculate the Hg in the original solution,  $m_{Hg}$ , as follows:

$$m_{Hg} = [C_{Hg(AC)}(DF)(V_f)(10^{-3})]/S \quad \text{Eq. 101-1}$$

Where:

$C_{Hg(AC)}$  = Total ng of Hg in aliquot analyzed (reagent blank subtracted).

DF = Dilution factor for the Hg-containing solution (before adding to the aeration cell; e.g., DF = 250/2 if the source samples were diluted as described in Section 11.2.2).

$V_f$  = Solution volume of original sample, 1000 ml for samples diluted as described in Section 11.2.1.

$10^{-3}$  = Conversion factor,  $\mu\text{g}/\text{ng}$ .

S = Aliquot volume added to aeration cell, ml.

12.4 Mercury Emission Rate.

Calculate the daily Hg emission rate, R,

using Equation 101-2. For continuous operations, the operating time is equal to 86,400 seconds per day. For cyclic operations, use only the time per day each stack is in operation. The total Hg emission rate from a source will be the summation of results from all stacks.

$$R = \frac{K_{m_{Hg}} V_s A_s (86,400 \times 10^{-6})}{[V_{m(\text{std})} + V_{w(\text{std})}](T_s/P_s)} \quad \text{Eq. 101-2}$$

Where:

$K_1 = 0.3858$   $^\circ\text{K}/\text{mm Hg}$  for metric units.

$K_1 = 17.64$   $^\circ\text{R}/\text{in. Hg}$  for English units.

$K_3 = 10^{-6}$  g/ $\mu$ g for metric units.

= 2.046 "  $\times 10^{-9}$  lb/ $\mu$ g for English units.

$P_s$  = Absolute stack gas pressure, mm Hg (in. Hg).

$t$  = Daily operating time, sec/day.

$T_s$  = Absolute average stack gas temperature,  $^{\circ}$ K ( $^{\circ}$ R).

$V_{m(std)}$  = Dry gas sample volume at standard conditions, scm (scf).

$V_{w(std)}$  = Volume of water vapor at standard conditions, scm (scf).

12.5 Determination of Compliance. Each performance test consists of three repetitions of the applicable test method. For the purpose of determining compliance with an applicable national emission standard, use the average of the results of all repetitions.

### 13.0 Method Performance

The following estimates are based on collaborative tests, wherein 13 laboratories performed duplicate analyses on two Hg-containing samples from a chlor-alkali plant and on one laboratory-prepared sample of known Hg concentration. The sample concentrations ranged from 2 to 65  $\mu$ g Hg/ml.

13.1 Precision. The estimated intra-laboratory and inter-laboratory standard deviations are 1.6 and 1.8  $\mu$ g Hg/ml, respectively.

13.2 Accuracy. The participating laboratories that analyzed a 64.3  $\mu$ g Hg/

ml (in 0.1 M ICl) standard obtained a mean of 63.7  $\mu$ g Hg/ml.

13.3 Analytical Range. After initial dilution, the range of this method is 0.5 to 120  $\mu$ g Hg/ml. The upper limit can be extended by further dilution of the sample.

14.0 Pollution Prevention. [Reserved]

15.0 Waste Management. [Reserved]

### 16.0 References

Same as Method 5, Section 17.0, References 1–3, 5, and 6, with the addition of the following:

1. Determining Dust Concentration in a Gas Stream. ASME Performance Test Code No. 27. New York, NY. 1957.

2. DeVorkin, Howard, *et al.* Air Pollution Source Testing Manual. Air Pollution Control District. Los Angeles, CA. November 1963.

3. Hatch, W.R., and W.I. Ott. Determination of Sub-Microgram Quantities of Mercury by Atomic Absorption Spectrophotometry. *Anal. Chem.* 40:2085–87. 1968.

4. Mark, L.S. Mechanical Engineers' Handbook. McGraw-Hill Book Co., Inc. New York, NY. 1951.

5. Western Precipitation Division of Joy Manufacturing Co. Methods for Determination of Velocity, Volume, Dust and Mist Content of Gases. Bulletin WP-50. Los Angeles, CA. 1968.

6. Perry, J.H. Chemical Engineers' Handbook. McGraw-Hill Book Co., Inc. New York, NY. 1960.

7. Shigehara, R.T., W.F. Todd, and W.S. Smith. Significance of Errors in Stack

Sampling Measurements. *Stack Sampling News.* 1(3):6–18. September 1973.

8. Smith, W.S., R.T. Shigehara, and W.F. Todd. A Method of Interpreting Stack Sampling Data. *Stack Sampling News.* 1(2):8–17. August 1973.

9. Standard Method for Sampling Stacks for Particulate Matter. In: 1971 Annual Book of ASTM Standards, Part 23. ASTM Designation D 2928–71. Philadelphia, PA 1971.

10. Vennard, J.K. Elementary Fluid Mechanics. John Wiley and Sons, Inc. New York. 1947.

11. Mitchell, W.J. and M.R. Midgett. Improved Procedure for Determining Mercury Emissions from Mercury Cell Chlor-Alkali Plants. *J. APCA.* 26:674–677. July 1976.

12. Shigehara, R.T. Adjustments in the EPA Nomograph for Different Pitot Tube Coefficients and Dry Molecular Weights. *Stack Sampling News.* 2:4–11. October 1974.

13. Vollaro, R.F. Recommended Procedure for Sample Traverses in Ducts Smaller than 12 Inches in Diameter. U.S. Environmental Protection Agency, Emission Measurement Branch. Research Triangle Park, NC. November 1976.

14. Klein, R. and C. Hach. Standard Additions: Uses and Limitation in Spectrophotometric Measurements. *Amer. Lab.* 9:21. 1977.

15. Perkin Elmer Corporation. Analytical Methods for Atomic Absorption Spectrophotometry. Norwalk, Connecticut. September 1976.

**BILLING CODE 6560–50–P**

## 17.0 Tables, Diagrams, Flowcharts, and Validation Data

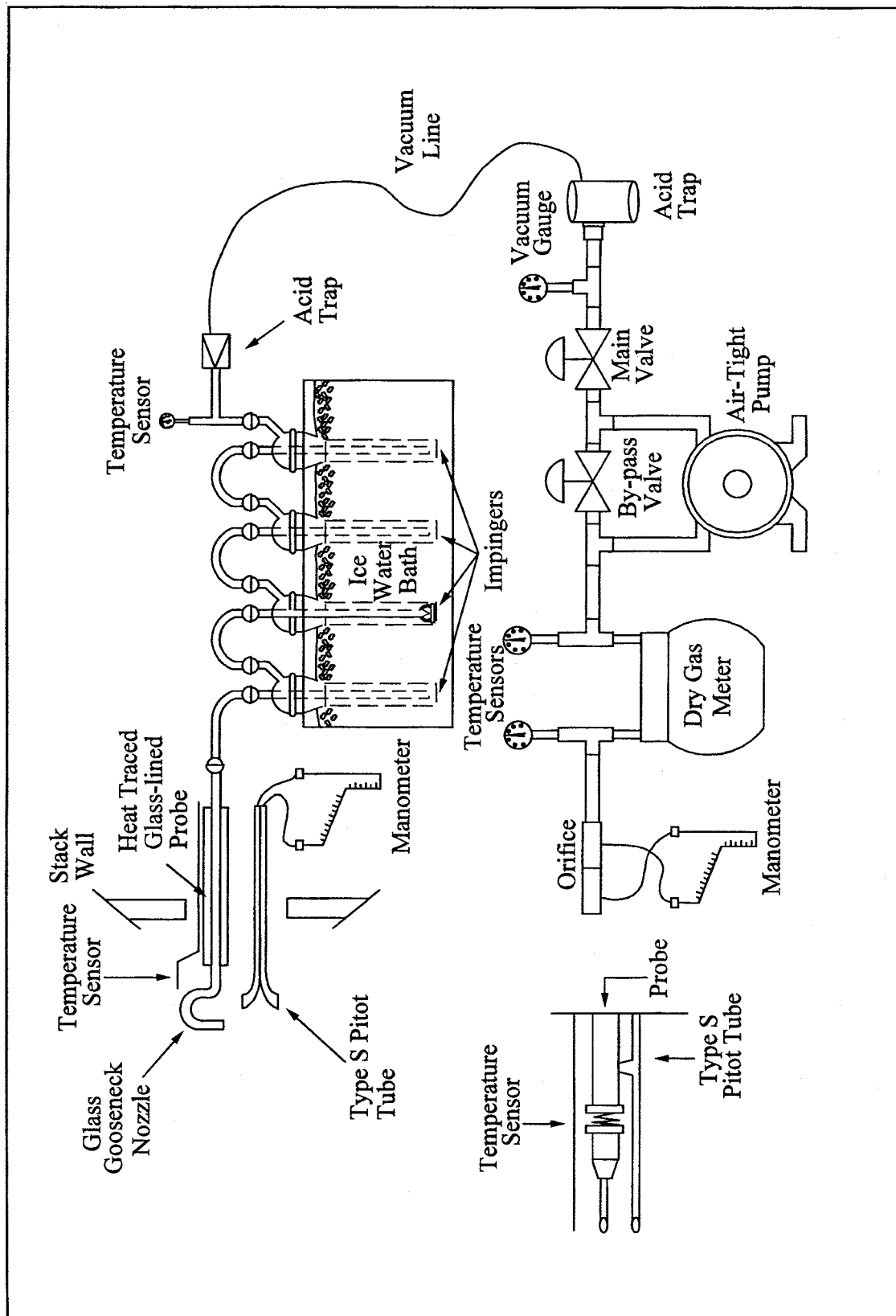


Figure 101-1. Mercury Sampling Train.

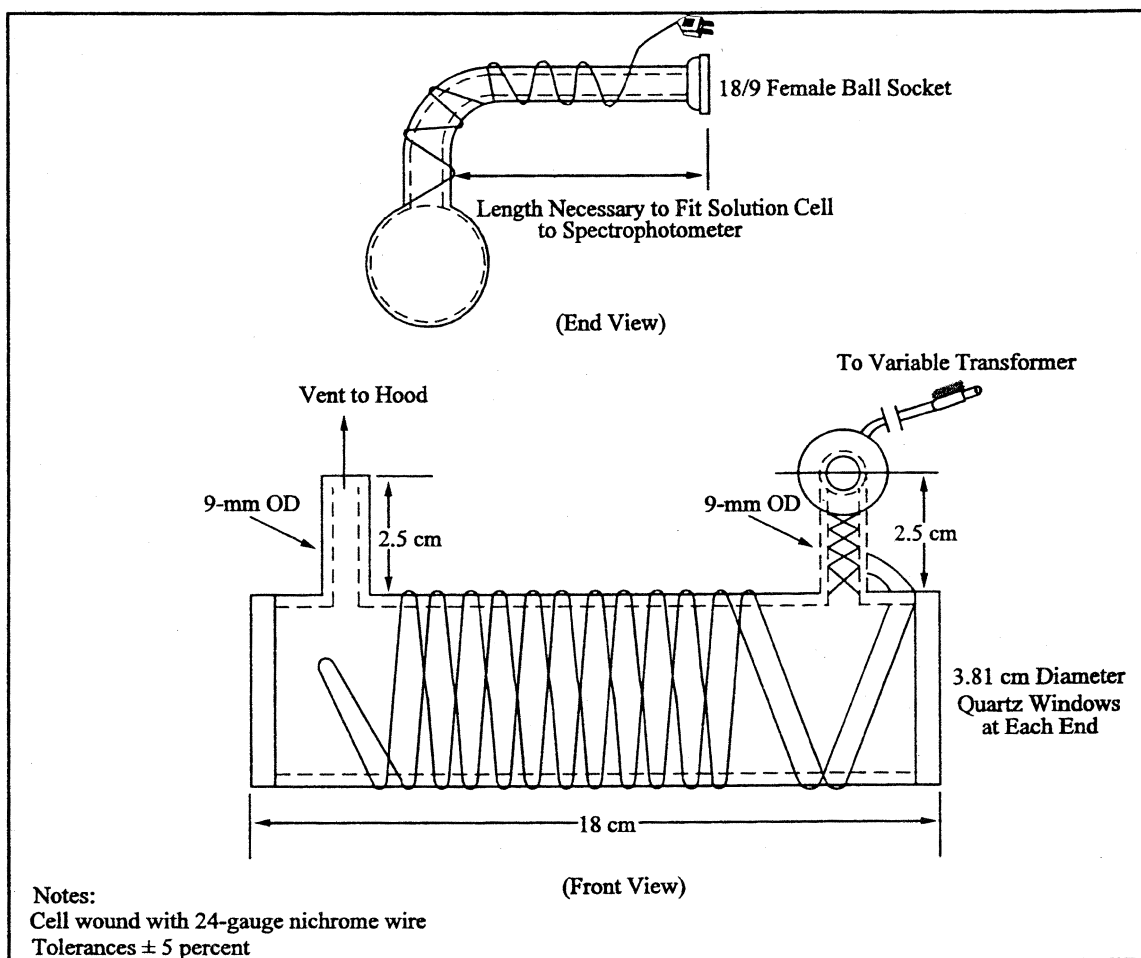


Figure 101-2. Optical Cell.

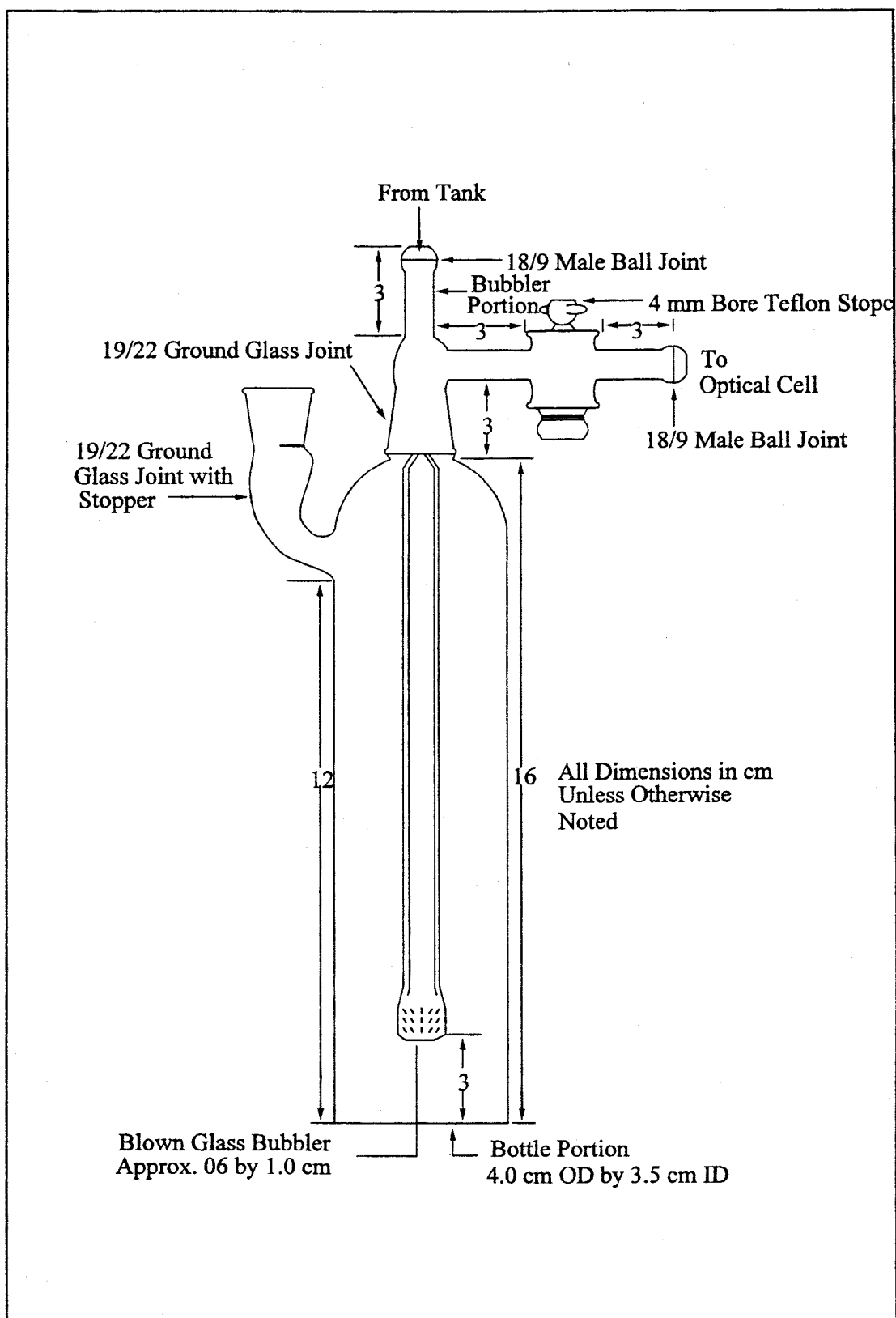
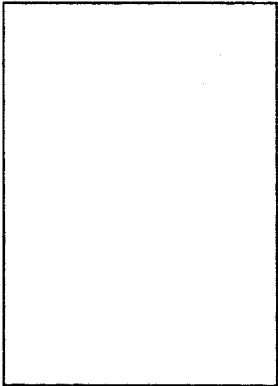


Figure 101-3. Aeration Cell.

Plant _____ Location _____ Operator _____ Date _____ Run No. _____ Sample box No. _____ Filter box No. _____ Meter H <sub>2</sub> O _____ C factor _____ Pitot tube coefficient, C <sub>p</sub> _____	Ambient temperature _____ Barometric pressure _____ Assumed moisture, % _____ Probe length, (ft.) _____ Nozzle identification No. _____ Average calibrated nozzle diameter, (in.) _____ Probe heater setting _____ Leak rate, (cfm) _____ Probe liner material _____ Static pressure, (in. Hg) _____ Filter No. _____	SCHEMATIC OF STACK CROSS SECTION 	Gas meter reading (ft <sup>3</sup> ) _____ Pressure differential across orifice meter (in. H <sub>2</sub> O) _____ Velocity head (ΔP <sub>v</sub> ) (in. H <sub>2</sub> O) _____ Stack temperature (T <sub>s</sub> ) (°F) _____ Vacuum (in. Hg) _____ Sampling time min. _____	Gas sample temperature at dry gas meter Inlet (°F) _____ Outlet (°F) _____ Filter holder* temperature (°F) _____ Temperature of gas leaving condenser or last impinger (°F) _____
Total	Avg.	Avg.	Avg.	Avg.
Average	Avg.	Avg.	Avg.	Avg.

\* If Applicable

Figure 101-4. Mercury Field Data.

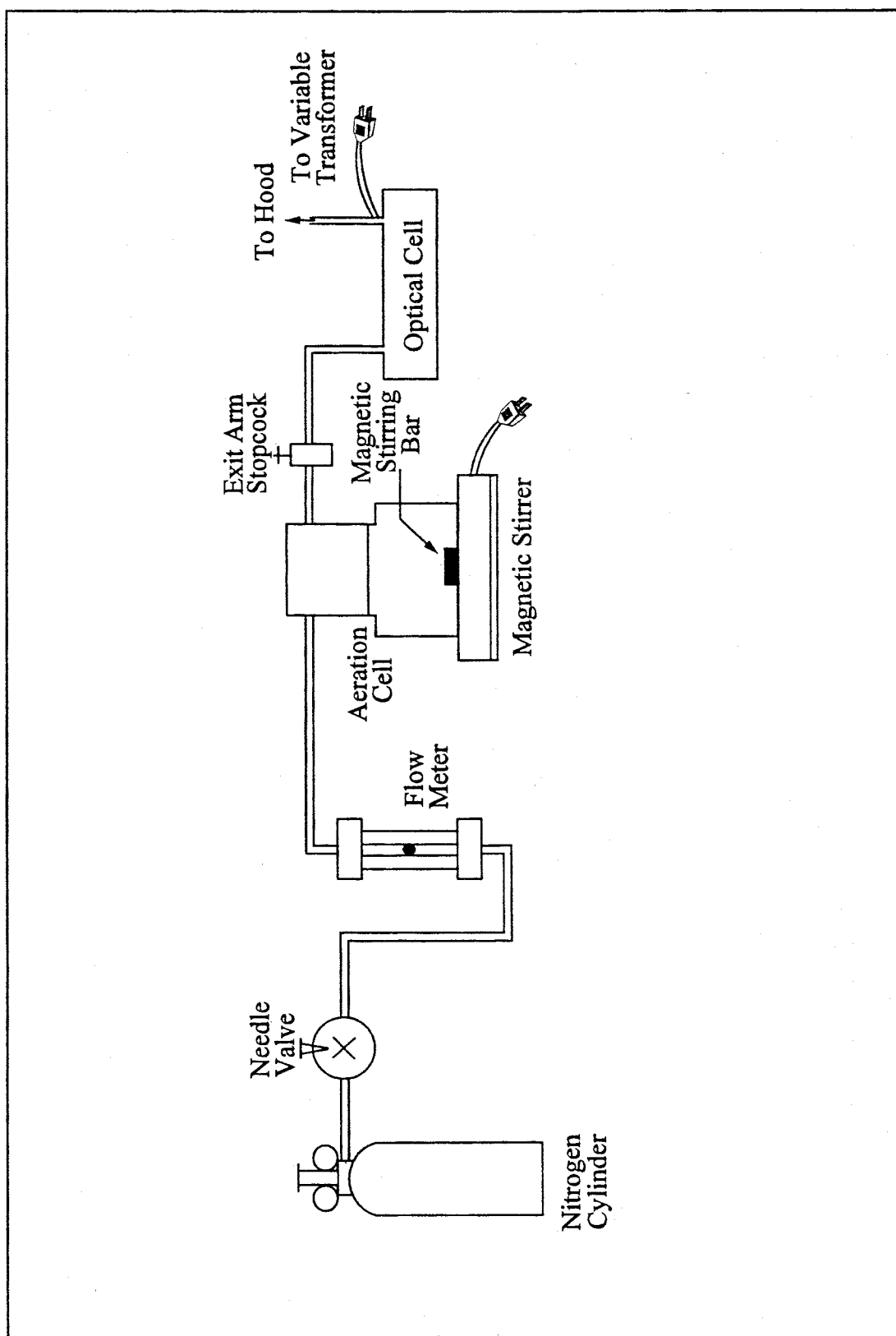


Figure 101-5. Schematic of Aeration System.

# Method 101A—Determination of Particulate and Gaseous Mercury Emissions From Sewage Sludge Incinerators

**Note:** This method does not include all of the specifications (e.g., equipment and

supplies) and procedures (e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from methods in Appendix A to 40 CFR Part 60 and in this part. Therefore, to obtain reliable results, persons using this method should also have a thorough knowledge of at least

the following additional test methods: Methods 1, Method 2, Method 3, and Method 5 of Part 60 (Appendix A), and Method 101 Part 61 (Appendix B).

## 1.0 Scope and Application

### 1.1 Analytes.

Analyte	CAS No.	Sensitivity
Mercury (Hg) .....	7439-97-6	Dependent upon spectrophotometer and recorder.

1.2 Applicability. This method is applicable for the determination of Hg emissions from sewage sludge incinerators and other sources as specified in an applicable subpart of the regulations.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

## 2.0 Summary of Method

2.1 Particulate and gaseous Hg emissions are withdrawn isokinetically from the source and are collected in acidic potassium permanganate (KMnO<sub>4</sub>) solution. The Hg collected (in the mercuric form) is reduced to elemental Hg, which is then aerated from the solution into an optical cell and measured by atomic absorption spectrophotometry.

## 3.0 Definitions. [Reserved]

## 4.0 Interferences

4.1 Sample Collection. Excessive oxidizable organic matter in the stack gas prematurely depletes the KMnO<sub>4</sub> solution and thereby prevents further collection of Hg.

4.2 Analysis. Condensation of water vapor on the optical cell windows causes a positive interference.

## 5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrochloric Acid (HCl). Highly toxic. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or edema of lungs. Exposure to concentrations of 0.13 to 0.2 percent can be lethal to humans in a few minutes. Provide ventilation to limit exposure. Reacts with metals, producing hydrogen gas.

5.2.2 Nitric Acid (HNO<sub>3</sub>). Highly corrosive to eyes, skin, nose, and lungs. Vapors cause bronchitis, pneumonia, or edema of lungs. Reaction to inhalation may be delayed as long as 30 hours and still be fatal. Provide ventilation to limit exposure. Strong oxidizer. Hazardous reaction may occur with organic materials such as solvents.

5.2.3 Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 3 mg/m<sup>3</sup> will cause lung damage in uninitiated. 1 mg/m<sup>3</sup> for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

5.3 Chlorine Evolution. Hydrochloric acid reacts with KMnO<sub>4</sub> to liberate chlorine gas. Although this is a minimal concern when small quantities of HCl (5–10 ml) are used in the impinger rinse, a potential safety hazard may still exist. At sources that emit higher concentrations of oxidizable materials (e.g., power plants), more HCl may be required to remove the larger amounts of brown deposit formed in the impingers. In such cases, the potential safety hazards due to sample container pressurization are greater, because of the larger volume of HCl rinse added to the recovered sample. These hazards are eliminated by storing and analyzing the HCl impinger wash separately from the permanganate impinger sample.

## 6.0 Equipment and Supplies

6.1 Sample Collection and Sample Recovery. Same as Method 101,

Sections 6.1 and 6.2, respectively, with the following exceptions:

6.1.1 Probe Liner. Same as in Method 101, Section 6.1.2, except that if a filter is used ahead of the impingers, the probe heating system must be used to minimize the condensation of gaseous Hg.

6.1.2 Filter Holder (Optional). Borosilicate glass with a rigid stainless-steel wire-screen filter support (do not use glass frit supports) and a silicone rubber or Teflon gasket, designed to provide a positive seal against leakage from outside or around the filter. The filter holder must be equipped with a filter heating system capable of maintaining a temperature around the filter holder of 120 ± 14 °C (248 ± 25 °F) during sampling to minimize both water and gaseous Hg condensation. A filter may also be used in cases where the stream contains large quantities of particulate matter.

6.2 Sample Analysis. Same as Method 101, Section 6.3, with the following additions and exceptions:

6.2.1 Volumetric Pipets. Class A; 1-, 2-, 3-, 4-, 5-, 10-, and 20-ml.

6.2.2 Graduated Cylinder. 25-ml.

6.2.3 Steam Bath.

6.2.4 Atomic Absorption Spectrophotometer or Equivalent. Any atomic absorption unit with an open sample presentation area in which to mount the optical cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. Instruments designed specifically for the measurement of mercury using the cold-vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

6.2.5 Optical Cell. Alternatively, a heat lamp mounted above the cell or a moisture trap installed upstream of the cell may be used.

6.2.6 Aeration Cell. Alternatively, aeration cells available with commercial cold vapor instrumentation may be used.

6.2.7 Aeration Gas Cylinder. Nitrogen, argon, or dry, Hg-free air, equipped with a single-stage regulator. Alternatively, aeration may be provided

by a peristaltic metering pump. If a commercial cold vapor instrument is used, follow the manufacturer's recommendations.

#### 7.0 Reagents and Standards

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Collection and Recovery. The following reagents are required for sample collection and recovery:

7.1.1 Water. Deionized distilled, to conform to ASTM D 1193-77 or 91 Type 1. If high concentrations of organic matter are not expected to be present, the analyst may eliminate the  $\text{KMnO}_4$  test for oxidizable organic matter. Use this water in all dilutions and solution preparations.

7.1.2 Nitric Acid, 50 Percent (V/V). Mix equal volumes of concentrated  $\text{HNO}_3$  and water, being careful to add the acid to the water slowly.

7.1.3 Silica Gel. Indicating type, 6 to 16 mesh. If previously used, dry at 175 °C (350 °F) for 2 hours. New silica gel may be used as received.

7.1.4 Filter (Optional). Glass fiber filter, without organic binder, exhibiting at least 99.95 percent efficiency on 0.3- $\mu\text{m}$  dioctyl phthalate smoke particles. The filter in cases where the gas stream contains large quantities of particulate matter, but blank filters should be analyzed for Hg content.

7.1.5 Sulfuric Acid, 10 Percent (V/V). Carefully add and mix 100 ml of concentrated  $\text{H}_2\text{SO}_4$  to 900 ml of water.

7.1.6 Absorbing Solution, 4 Percent  $\text{KMnO}_4$  (W/V). Prepare fresh daily. Dissolve 40 g of  $\text{KMnO}_4$  in sufficient 10 percent  $\text{H}_2\text{SO}_4$  to make 1 liter. Prepare and store in glass bottles to prevent degradation.

7.1.7 Hydrochloric Acid, 8 N. Carefully add and mix 67 ml of concentrated  $\text{HCl}$  to 33 ml of water.

7.2 Sample Analysis. The following reagents and standards are required for sample analysis:

7.2.1 Water. Same as in Section 7.1.1.

7.2.2 Tin (II) Solution. Prepare fresh daily, and keep sealed when not being used. Completely dissolve 20 g of tin (II) chloride (or 25 g of tin (II) sulfate) crystals (Baker Analyzed reagent grade or any other brand that will give a clear solution) in 25 ml of concentrated  $\text{HCl}$ . Dilute to 250 ml with water. Do not substitute  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ , or other strong acids for the  $\text{HCl}$ .

7.2.3 Sodium Chloride-Hydroxylamine Solution. Dissolve 12 g

of sodium chloride and 12 g of hydroxylamine sulfate (or 12 g of hydroxylamine hydrochloride) in water and dilute to 100 ml.

7.2.4 Hydrochloric Acid, 8 N. Same as Section 7.1.7.

7.2.5 Nitric Acid, 15 Percent (V/V). Carefully add 15 ml  $\text{HNO}_3$  to 85 ml of water.

7.2.6 Antifoam B Silicon Emulsion. J.T. Baker Company (or equivalent).

7.2.7 Mercury Stock Solution, 1 mg Hg/ml. Prepare and store all Hg standard solutions in borosilicate glass containers. Completely dissolve 0.1354 g of Hg (II) chloride in 75 ml of water. Add 10 ml of concentrated  $\text{HNO}_3$ , and adjust the volume to exactly 100 ml with water. Mix thoroughly. This solution is stable for at least one month.

7.2.8 Intermediate Hg Standard Solution, 10  $\mu\text{g}/\text{ml}$ . Prepare fresh weekly. Pipet 5.0 ml of the Hg stock solution (Section 7.2.7) into a 500 ml volumetric flask, and add 20 ml of 15 percent  $\text{HNO}_3$  solution. Adjust the volume to exactly 500 ml with water. Thoroughly mix the solution.

7.2.9 Working Hg Standard Solution, 200 ng Hg/ml. Prepare fresh daily. Pipet 5.0 ml from the "Intermediate Hg Standard Solution" (Section 7.2.8) into a 250-ml volumetric flask. Add 5 ml of 4 percent  $\text{KMnO}_4$  absorbing solution and 5 ml of 15 percent  $\text{HNO}_3$ . Adjust the volume to exactly 250 ml with water. Mix thoroughly.

7.2.10 Potassium Permanganate, 5 Percent (W/V). Dissolve 5 g of  $\text{KMnO}_4$  in water and dilute to 100 ml.

7.2.11 Filter. Whatman No. 40, or equivalent.

#### 8.0 Sample Collection, Preservation, Transport, and Storage

Same as Method 101, Section 8.0, with the exception of the following:

8.1 Preliminary Determinations. Same as Method 101, Section 8.2, except that the liberation of free iodine in the first impinger due to high Hg or sulfur dioxide concentrations is not applicable. In this method, high oxidizable organic content may make it impossible to sample for the desired minimum time. This problem is indicated by the complete bleaching of the purple color of the  $\text{KMnO}_4$  solution. In cases where an excess of water condensation is encountered, collect two runs to make one sample, or add an extra impinger in front of the first impinger (also containing acidified  $\text{KMnO}_4$  solution).

8.2 Preparation of Sampling Train. Same as Method 101, Section 8.3, with the exception of the following:

8.2.1 In this method, clean all the glass components by rinsing with 50

percent  $\text{HNO}_3$ , tap water, 8 N  $\text{HCl}$ , tap water, and finally with deionized distilled water. Then place 50 ml of absorbing solution in the first impinger and 100 ml in each of the second and third impingers.

8.2.2 If a filter is used, use a pair of tweezers to place the filter in the filter holder. Be sure to center the filter, and place the gasket in the proper position to prevent the sample gas stream from bypassing the filter. Check the filter for tears after assembly is completed. Be sure also to set the filter heating system at the desired operating temperature after the sampling train has been assembled.

8.3 Sampling Train Operation. In addition to the procedure outlined in Method 101, Section 8.5, maintain a temperature around the filter (if applicable) of  $120 \pm 14$  °C ( $248 \pm 25$  °F).

8.4 Sample Recovery. Same as Method 101, Section 8.7, with the exception of the following:

8.4.1 Transfer the probe, impinger assembly, and (if applicable) filter assembly to the cleanup area.

8.4.2 Treat the sample as follows:

8.4.2.1 Container No. 1 (Impinger, Probe, and Filter Holder) and, if applicable, Container No. 1A ( $\text{HCl}$  rinse).

8.4.2.1.1 Using a graduated cylinder, measure the liquid in the first three impingers to within 1 ml. Record the volume of liquid present (e.g., see Figure 5-6 of Method 5). This information is needed to calculate the moisture content of the effluent gas. (Use only graduated cylinder and glass storage bottles that have been precleaned as in Section 8.2.1.) Place the contents of the first three impingers (four if an extra impinger was added as described in Section 8.1) into a 1000-ml glass sample bottle labeled Container No. 1.

**Note:** If a filter is used, remove the filter from its holder as outlined under Section 8.4.3.

8.4.2.1.2 Taking care that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover the Hg (and any condensate) from the probe nozzle, probe fitting, probe liner, front half of the filter holder (if applicable), and impingers as follows: Rinse these components with a total of 400 ml (350 ml if an extra impinger was added as described in Section 8.1) of fresh absorbing solution, carefully assuring removal of all loose particulate matter from the impingers; add all washings to the 1000 ml glass sample bottle. To remove any residual brown deposits on the glassware following the

permanganate rinse, rinse with approximately 100 ml of water, carefully assuring removal of all loose particulate matter from the impingers. Add this rinse to Container No. 1.

8.4.2.1.3 If no visible deposits remain after this water rinse, do not rinse with 8 N HCl. If deposits do remain on the glassware after the water rinse, wash impinger walls and stems with 25 ml of 8 N HCl, and place the wash in a separate container labeled Container No. 1A as follows: Place 200 ml of water in a sample container labeled Container No. 1A. Wash the impinger walls and stem with the HCl by turning the impinger on its side and rotating it so that the HCl contacts all inside surfaces. Pour the HCl wash carefully with stirring into Container No. 1A.

8.4.2.1.4 After all washings have been collected in the appropriate sample container(s), tighten the lid(s) on

the container(s) to prevent leakage during shipment to the laboratory. Mark the height of the fluid level to allow subsequent determination of whether leakage has occurred during transport. Label each container to identify its contents clearly.

8.4.3 Container No. 2 (Silica Gel). Same as Method 5, Section 8.7.6.3.

8.4.4 Container No. 3 (Filter). If a filter was used, carefully remove it from the filter holder, place it in a 100-ml glass sample bottle, and add 20 to 40 ml of absorbing solution. If it is necessary to fold the filter, be sure that the particulate cake is inside the fold. Carefully transfer to the 100-ml sample bottle any particulate matter and filter fibers that adhere to the filter holder gasket by using a dry Nylon bristle brush and a sharp-edged blade. Seal the container. Label the container to identify its contents clearly. Mark the height of the fluid level to allow

subsequent determination of whether leakage has occurred during transport.

8.4.5 Container No. 4 (Filter Blank). If a filter was used, treat an unused filter from the same filter lot as that used for sampling according to the procedures outlined in Section 8.4.4.

8.4.6 Container No. 5 (Absorbing Solution Blank). Place 650 ml of 4 percent  $\text{KMnO}_4$  absorbing solution in a 1000-ml sample bottle. Seal the container.

8.4.7 Container No. 6 (HCl Rinse Blank). Place 200 ml of water in a 1000-ml sample bottle, and add 25 ml of 8 N HCl carefully with stirring. Seal the container. Only one blank sample per 3 runs is required.

## 9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.0, 10.0 .....	Sampling equipment leak-checks and calibration .....	Ensure accuracy and precision of sampling measurements.
10.2 .....	Spectrophotometer calibration .....	Ensure linearity of spectrophotometer response to standards.
11.3.3 .....	Check for matrix effects .....	Eliminate matrix effects.

9.2 Volume Metering System Checks. Same as Method 5, Section 9.2.

## 10.0 Calibration and Standardization

Same as Method 101, Section 10.0, with the following exceptions:

10.1 Optical Cell Heating System Calibration. Same as in Method 101, Section 10.4, except use a 25 ml graduated cylinder to add 25 ml of water to the bottle section of the aeration cell.

10.2 Spectrophotometer and Recorder Calibration.

10.2.1 The Hg response may be measured by either peak height or peak area.

**Note:** The temperature of the solution affects the rate at which elemental Hg is released from a solution and, consequently, it affects the shape of the absorption curve (area) and the point of maximum absorbance (peak height). To obtain reproducible results, all solutions must be brought to room temperature before use.

10.2.2 Set the spectrophotometer wave length at 253.7 nm, and make certain the optical cell is at the minimum temperature that will prevent water condensation. Then set the recorder scale as follows: Using a 25-ml graduated cylinder, add 25 ml of water to the aeration cell bottle. Add three drops of Antifoam B to the bottle, and then pipet 5.0 ml of the working Hg standard solution into the aeration cell.

**Note:** Always add the Hg-containing solution to the aeration cell after the 25 ml of water.

10.2.3 Place a Teflon-coated stirring bar in the bottle. Add 5 ml of absorbing solution to the aeration bottle, and mix well. Before attaching the bottle section to the bubbler section of the aeration cell, make certain that (1) the aeration cell exit arm stopcock (Figure 101-3 of Method 101) is closed (so that Hg will not prematurely enter the optical cell when the reducing agent is being added) and (2) there is no flow through the bubbler. If conditions (1) and (2) are met, attach the bottle section to the bubbler section of the aeration cell. Add sodium chloride-hydroxylamine in 1 ml increments until the solution is colorless. Now add 5 ml of tin (II) solution to the aeration bottle through the side arm, and immediately stopper the side arm. Stir the solution for 15 seconds, turn on the recorder, open the aeration cell exit arm stopcock, and immediately initiate aeration with continued stirring. Determine the maximum absorbance of the standard, and set this value to read 90 percent of the recorder full scale.

## 11.0 Analytical Procedure

11.1 Sample Loss Check. Check the liquid level in each container to see if liquid was lost during transport. If a noticeable amount of leakage occurred, either void the sample or use methods

subject to the approval of the Administrator to account for the losses.

11.2 Sample Preparation. Treat sample containers as follows:

11.2.1 Containers No. 3 and No. 4 (Filter and Filter Blank).

11.2.1.1 If a filter is used, place the contents, including the filter, of Containers No. 3 and No. 4 in separate 250-ml beakers, and heat the beakers on a steam bath until most of the liquid has evaporated. Do not heat to dryness. Add 20 ml of concentrated  $\text{HNO}_3$  to the beakers, cover them with a watch glass, and heat on a hot plate at 70 °C (160 °F) for 2 hours. Remove from the hot plate.

11.2.1.2 Filter the solution from digestion of the Container No. 3 contents through Whatman No. 40 filter paper, and save the filtrate for addition to the Container No. 1 filtrate as described in Section 11.2.2. Discard the filter paper.

11.2.1.3 Filter the solution from digestion of the Container No. 4 contents through Whatman No. 40 filter paper, and save the filtrate for addition to Container No. 5 filtrate as described in Section 11.2.3 below. Discard the filter paper.

11.2.2 Container No. 1 (Impingers, Probe, and Filter Holder) and, if applicable, No. 1A (HCl rinse).

11.2.2.1 Filter the contents of Container No. 1 through Whatman No. 40 filter paper into a 1 liter volumetric flask to remove the brown manganese

dioxide (MnO<sub>2</sub>) precipitate. Save the filter for digestion of the brown MnO<sub>2</sub> precipitate. Add the sample filtrate from Container No. 3 to the 1-liter volumetric flask, and dilute to volume with water. If the combined filtrates are greater than 1000 ml, determine the volume to the nearest ml and make the appropriate corrections for blank subtractions. Mix thoroughly. Mark the filtrate as analysis Sample No. A.1 and analyze for Hg within 48 hr of the filtration step. Place the saved filter, which was used to remove the brown MnO<sub>2</sub> precipitate, into an appropriate sized container. In a laboratory hood, add 25 ml of 8 N HCl to the filter and allow to digest for a minimum of 24 hours at room temperature.

11.2.2.2 Filter the contents of Container 1A through Whatman No. 40 filter paper into a 500-ml volumetric flask. Then filter the digestate of the brown MnO<sub>2</sub> precipitate from Container No. 1 through Whatman No. 40 filter paper into the same 500-ml volumetric flask, and dilute to volume with water. Mark this combined 500 ml dilute solution as analysis Sample No. A.2. Discard the filters.

11.2.3 Container No. 5 (Absorbing Solution Blank) and No. 6 (HCl Rinse Blank).

11.2.3.1 Treat Container No. 5 as Container No. 1 (as described in Section 11.2.2), except substitute the filter blank filtrate from Container No. 4 for the sample filtrate from Container No. 3, and mark as Sample A.1 Blank.

11.2.3.2 Treat Container No. 6 as Container No. 1A, (as described in Section 11.2.2, except substitute the filtrate from the digested blank MnO<sub>2</sub> precipitate for the filtrate from the digested sample MnO<sub>2</sub> precipitate, and mark as Sample No. A.2 Blank.

**Note:** When analyzing samples A.1 Blank and HCl A.2 Blank, always begin with 10 ml aliquots. This applies specifically to blank samples.

11.3 Analysis. Calibrate the analytical equipment and develop a calibration curve as outlined in Section 10.0.

11.3.1 Mercury Samples. Then repeat the procedure used to establish the calibration curve with appropriately sized aliquots (1 to 10 ml) of the samples (from Sections 11.2.2 and 11.2.3) until two consecutive peak heights agree within 3 percent of their average value. If the 10 ml sample is below the detectable limit, use a larger aliquot (up to 20 ml), but decrease the volume of water added to the aeration cell accordingly to prevent the solution volume from exceeding the capacity of the aeration bottle. If the peak maximum of a 1.0 ml aliquot is off scale, further dilute the original sample to bring the Hg concentration into the calibration range of the spectrophotometer. If the Hg content of the absorbing solution and filter blank is below the working range of the analytical method, use zero for the blank.

11.3.2 Run a blank and standard at least after every five samples to check the spectrophotometer calibration; recalibrate as necessary.

11.3.3 Check for Matrix Effects (optional). Same as Method 101, Section 11.3.3.

## 12.0 Data Analysis and Calculations

**Note:** Carry out calculations, retaining at least one extra decimal significant figure beyond that of the acquired data. Round off figures only after the final calculation. Other forms of the equations may be used as long as they give equivalent results.

### 12.1 Nomenclature.

$C_{(ftr)Hg}$  = Total ng of Hg in aliquot of KMnO<sub>4</sub> filtrate and HNO<sub>3</sub> digestion of filter analyzed (aliquot of analysis Sample No. A.1).

$C_{(ftr\ blank)Hg}$  = Total ng of Hg in aliquot of KMnO<sub>4</sub> blank and HNO<sub>3</sub> digestion of blank filter analyzed (aliquot of analysis Sample No. A.1 blank).

$C_{(HCl\ blank)Hg}$  = Total ng of Hg analyzed in aliquot of the 500-ml analysis Sample No. HCl A.2 blank.

$C_{(HCl)Hg}$  = Total ng of Hg analyzed in the aliquot from the 500-ml analysis Sample No. HCl A.2.

DF = Dilution factor for the HCl-digested Hg-containing solution, Analysis Sample No. "HCl A.2."

$DF_{blk}$  = Dilution factor for the HCl-digested Hg containing solution, Analysis Sample No. "HCl A.2 blank." (Refer to sample No. "HCl A.2" dilution factor above.)

$m_{(ftr)Hg}$  = Total blank corrected µg of Hg in KMnO<sub>4</sub> filtrate and HNO<sub>3</sub> digestion of filter sample.

$m_{(HCl)Hg}$  = Total blank corrected µg of Hg in HCl rinse and HCl digestate of filter sample.

$m_{Hg}$  = Total blank corrected Hg content in each sample, µg.

S = Aliquot volume of sample added to aeration cell, ml.

$S_{blk}$  = Aliquot volume of blank added to aeration cell, ml.

$V_{f(blk)}$  = Solution volume of blank sample, 1000 ml for samples diluted as described in Section 11.2.2.

$V_{f(ftr)}$  = Solution volume of original sample, normally 1000 ml for samples diluted as described in Section 11.2.2.

$V_{f(HCl)}$  = Solution volume of original sample, 500 ml for samples diluted as described in Section 11.2.1.

$10^{-3}$  = Conversion factor, µg/ng.

12.2 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop, Dry Gas Volume, Volume of Water Vapor Condensed, Moisture Content, Isokinetic Variation, and Stack Gas Velocity and Volumetric Flow Rate. Same as Method 5, Sections 12.2 through 12.5, 12.11, and 12.12, respectively.

### 12.3 Total Mercury.

12.3.1 For each source sample, correct the average maximum absorbance of the two consecutive samples whose peak heights agree within 3 percent of their average for the contribution of the blank. Use the calibration curve and these corrected averages to determine the final total weight of Hg in ng in the aeration cell for each source sample.

12.3.2 Correct for any dilutions made to bring the sample into the working range of the spectrophotometer.

$$m_{(HCl)Hg} = \frac{[C_{(HCl)Hg} DF]}{S} - \frac{[C_{(HCl)Hg} DF_{blk}]}{S_{blk}} V_{f(HCl)} (10^{-3}) \quad \text{Eq. 101A-1}$$

**Note:** This dilution factor applies only to the intermediate dilution steps, since the original sample volume [(V)<sub>HCL</sub>] of "HCl A.2" has been factored out in the equation along with the sample aliquot (S). In Eq. 101A-1, the sample aliquot, S, is introduced directly into the aeration cell for analysis

according to the procedure outlined in Section 11.3.1. A dilution factor is required only if it is necessary to bring the sample into the analytical instrument's calibration range.

**Note:** The maximum allowable blank subtraction for the HCl is the lesser of the two following values: (1) the actual blank

measured value (analysis Sample No. HCl A.2 blank), or (2) 5% of the Hg content in the combined HCl rinse and digested sample (analysis Sample No. HCl A.2).

$$m_{(filtr)Hg} = \frac{[C_{(filtr)Hg} DF V_{f(filtr)}]}{S} - \frac{[C_{(filtr\ blk)Hg} DF_{blk} V_{f(blk)}]}{S_{blk}}$$

Eq. 101A-2

**Note:** The maximum allowable blank subtraction for the HCl is the lesser of the

two following values: (1) the actual blank measured value (analysis Sample No. "A.1

blank"), or (2) 5% of the Hg content in the filtrate (analysis Sample No. "A.1").

$$m_{Hg} = m_{(HCl)Hg} + m_{(filtr)Hg}$$

Eq. 101A-3

12.3 Mercury Emission Rate. Same as Method 101, Section 12.3.

12.4 Determination of Compliance. Same as Method 101, Section 12.4.

13.0 Method Performance

13.1 Precision. Based on eight paired-train tests, the intra-laboratory standard deviation was estimated to be 4.8 µg/ml in the concentration range of 50 to 130 µg/m<sup>3</sup>.

13.2 Bias. [Reserved]

13.3 Range. After initial dilution, the range of this method is 20 to 800 ng Hg/ml. The upper limit can be extended by further dilution of the sample.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as Section 16.0 of Method 101, with the addition of the following:

1. Mitchell, W.J., *et al.* Test Methods to Determine the Mercury Emissions from Sludge Incineration Plants. U.S. Environmental Protection Agency. Research Triangle Park, NC. Publication No. EPA-600/4-79-058. September 1979.

2. Wilshire, Frank W., *et al.* Reliability Study of the U.S. EPA's Method 101A—Determination of Particulate and Gaseous Mercury Emissions. U.S. Environmental Protection Agency. Research Triangle Park, NC. Report No. 600/D-31/219 AREAL 367, NTIS Acc No. PB91-233361.

3. Memorandum from William J. Mitchell to Roger T. Shigehara discussing the potential safety hazard in Section 7.2 of Method 101A. February 28, 1990.

17.0 Tables, Diagrams, Flowcharts, And Validation Data [Reserved]

Method 102—Determination of Particulate and Gaseous Mercury Emissions From Chlor-Alkali Plants (Hydrogen Streams)

**Note:** This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part and in Appendix A to 40 CFR Part 60. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5, and Method 101.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Mercury (Hg) .....	7439-97-6	Dependent upon recorder and spectrophotometer.

1.2 Applicability. This method is applicable for the determination of Hg emissions, including both particulate and gaseous Hg, from chlor-alkali plants and other sources (as specified in the regulations) where the carrier-gas stream in the duct or stack is principally hydrogen.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 Particulate and gaseous Hg emissions are withdrawn isokinetically from the source and collected in acidic iodine monochloride (ICl) solution. The Hg collected (in the mercuric form) is reduced to elemental Hg, which is then aerated from the solution into an optical cell and measured by atomic absorption spectrophotometry.

3.0 Definitions [Reserved]

4.0 Interferences

Same as Method 101, Section 4.2.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. Same as Method 101, Section 5.2.

5.3 Explosive Mixtures. The sampler must conduct the source test under conditions of utmost safety because hydrogen and air mixtures are explosive. Since the sampling train essentially is leakless, attention to safe operation can be concentrated at the inlet and outlet. If a leak does occur, however, remove the meter box cover to avoid a possible explosive mixture. The following specific precautions are recommended:

5.3.1 Operate only the vacuum pump during the test. The other electrical equipment, *e.g.*, heaters, fans,

and timers, normally are not essential to the success of a hydrogen stream test.

5.3.2 Seal the sample port to minimize leakage of hydrogen from the stack.

5.3.3 Vent sampled hydrogen at least 3 m (10 ft) away from the train. This can be accomplished by attaching a 13-mm (0.50-in.) ID Tygon tube to the exhaust from the orifice meter.

**Note:** A smaller ID tubing may cause the orifice meter calibration to be erroneous. Take care to ensure that the exhaust line is not bent or pinched.

6.0 Equipment and Supplies

Same as Method 101, Section 6.0, with the exception of the following:

6.1 Probe Heating System. Do not use, unless otherwise specified.

6.2 Glass Fiber Filter. Do not use, unless otherwise specified.

7.0 Reagents and Standards

Same as Method 101, Section 7.0.

**8.0 Sample Collection, Preservation, Transport, and Storage**

Same as Method 101, Section 8.0, with the exception of the following:

**8.1 Setting of Isokinetic Rates.**

8.1.1 If a nomograph is used, take special care in the calculation of the molecular weight of the stack gas and in the setting of the nomograph to maintain isokinetic conditions during

sampling (Sections 8.1.1.1 through 8.1.1.3 below).

8.1.1.1 Calibrate the meter box orifice. Use the techniques described in APTD-0576 (see Reference 9 in Section 17.0 of Method 5). Calibration of the orifice meter at flow conditions that simulate the conditions at the source is suggested. Calibration should either be done with hydrogen or with some other gas having similar Reynolds Number so

that there is similarity between the Reynolds Numbers during calibration and during sampling.

8.1.1.2 The nomograph described in APTD-0576 cannot be used to calculate the C factor because the nomograph is designed for use when the stack gas dry molecular weight is  $29 \pm 4$ . Instead, the following calculation should be made to determine the proper C factor:

$$C = 0.00154 \Delta H @ C_p^2 T_m (P_s / P_m) \frac{(1 - B_{ws})^2}{(1 - B_{ws}) + 18 B_{ws}}$$

Eq. 102-1

Where:

$B_{ws}$  = Fraction by volume of water vapor in the stack gas.

$C_p$  = Pitot tube calibration coefficient, dimensionless.

$M_d$  = Dry molecular weight of stack gas, lb/lb-mole.

$P_s$  = Absolute pressure of stack gas, in. Hg.

$P_m$  = Absolute pressure of gas at the meter, in. Hg.

$T_m$  = Absolute temperature of gas at the orifice, °R.

$\Delta H @$  = Meter box calibration factor obtained in Section 8.1.1.1, in.  $H_2O$ .  $0.00154 = (\text{in. } H_2O / ^\circ R)$ .

**Note:** This calculation is left in English units, and is not converted to metric units because nomographs are based on English units.

8.1.1.3 Set the calculated C factor on the operating nomograph, and select the proper nozzle diameter and K factor as specified in APTD-0576. If the C factor obtained in Section 8.1.1.2 exceeds the

values specified on the existing operating nomograph, expand the C scale logarithmically so that the values can be properly located.

8.1.2 If a calculator is used to set isokinetic rates, it is suggested that the isokinetic equation presented in Reference 13 in Section 17.0 of Method 101 be consulted.

8.2 Sampling in Small (<12-in. Diameter) Stacks. When the stack diameter (or equivalent diameter) is less than 12 inches, conventional pitot tube-probe assemblies should not be used. For sampling guidelines, see Reference 14 in Section 17.0 of Method 101.

**9.0 Quality Control**

Same as Method 101, Section 9.0.

**10.0 Calibration and Standardizations**

Same as Method 101, Section 10.0.

**11.0 Analytical Procedure**

Same as Method 101, Section 11.0.

**12.0 Data Analysis and Calculations**

Same as Method 101, Section 12.0.

**13.0 Method Performance**

Same as Method 101, Section 13.0.

13.1 Analytical Range. After initial dilution, the range of this method is 0.5 to 120  $\mu\text{g Hg/ml}$ . The upper limit can be extended by further dilution of the sample.

**14.0 Pollution Prevention. [Reserved]****15.0 Waste Management. [Reserved]****16.0 References**

Same as Method 101, Section 16.0.

**17.0 Tables, Diagrams, Flowcharts, and Validation Data. [Reserved]****Method 103—Beryllium Screening Method****1.0 Scope and Application**

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Beryllium (Be) .....	7440-41-7	Dependent upon analytical procedure used.

1.2 Applicability. This procedure details guidelines and requirements for methods acceptable for use in determining Be emissions in ducts or stacks at stationary sources.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

**2.0 Summary of Method**

2.1 Particulate Be emissions are withdrawn isokinetically from three points in a duct or stack and are collected on a filter. The collected sample is analyzed for Be using an appropriate technique.

**3.0 Definitions. [Reserved]****4.0 Interferences. [Reserved]****5.0 Safety**

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Hydrochloric Acid (HCl). Highly corrosive and toxic. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or edema of

lungs. Exposure to concentrations of 0.13 to 0.2 percent can be lethal to humans in a few minutes. Provide ventilation to limit exposure. Reacts with metals, producing hydrogen gas. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burn as thermal burn.

**6.0 Equipment and Supplies**

6.1 Sample Collection. A schematic of the required sampling train configuration is shown in Figure 103-1 in Section 17.0. The essential components of the train are as follows:

6.1.1 Nozzle. Stainless steel, or equivalent, with sharp, tapered leading edge.

6.1.2 Probe. Sheathed borosilicate or quartz glass tubing.

6.1.3 Filter. Millipore AA, or equivalent, with appropriate filter holder that provides a positive seal against leakage from outside or around the filter. It is suggested that a Whatman 41, or equivalent, be placed immediately against the back side of the Millipore filter as a guard against breakage of the Millipore. Include the backup filter in the analysis. To be equivalent, other filters shall exhibit at least 99.95 percent efficiency (0.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles, and be amenable to the Be analysis procedure. The filter efficiency tests shall be conducted in accordance with ASTM D 2986-71, 78, 95a (incorporated by reference—see § 61.18). Test data from the supplier's quality control program are sufficient for this purpose.

6.1.4 Meter-Pump System. Any system that will maintain isokinetic sampling rate, determine sample volume, and is capable of a sampling rate of greater than 14 lpm (0.5 cfm).

6.2 Measurement of Stack Conditions. The following equipment is used to measure stack conditions:

6.2.1 Pitot Tube. Type S, or equivalent, with a constant coefficient ( $\pm 5$  percent) over the working range.

6.2.2 Inclined Manometer, or Equivalent. To measure velocity head to  $\pm 10$  percent of the minimum value.

6.2.3 Temperature Measuring Device. To measure stack temperature to  $\pm 1.5$  percent of the minimum absolute stack temperature.

6.2.4 Pressure Measuring Device. To measure stack pressure to  $\pm 2.5$  mm Hg (0.1 in. Hg).

6.2.5 Barometer. To measure atmospheric pressure to  $\pm 2.5$  mm Hg (0.1 in. Hg).

6.2.6 Wet and Dry Bulb Thermometers, Drying Tubes, Condensers, or Equivalent. To determine stack gas moisture content to  $\pm 1$  percent.

6.3 Sample Recovery.

6.3.1 Probe Cleaning Equipment. Probe brush or cleaning rod at least as long as probe, or equivalent. Clean cotton balls, or equivalent, should be used with the rod.

6.3.2 Leakless Glass Sample Bottles. To contain sample.

6.4 Analysis. All equipment necessary to perform an atomic absorption, spectrographic, fluorometric, chromatographic, or equivalent analysis.

## 7.0 Reagents and Standards

7.1 Sample Recovery.

7.1.1 Water. Deionized distilled, to conform to ASTM D 1193-77, 91 (incorporated by reference—see § 61.18), Type 3.

7.1.2 Acetone. Reagent grade.

7.1.3 Wash Acid, 50 Percent (V/V) Hydrochloric Acid (HCl). Mix equal volumes of concentrated HCl and water, being careful to add the acid slowly to the water.

7.2 Analysis. Reagents and standards as necessary for the selected analytical procedure.

## 8.0 Sample Collection, Preservation, Transport, and Storage

Guidelines for source testing are detailed in the following sections. These guidelines are generally applicable; however, most sample sites differ to some degree and temporary alterations such as stack extensions or expansions often are required to insure the best possible sample site. Further, since Be is hazardous, care should be taken to minimize exposure. Finally, since the total quantity of Be to be collected is quite small, the test must be carefully conducted to prevent contamination or loss of sample.

8.1 Selection of a Sampling Site and Number of Sample Runs. Select a suitable sample site that is as close as practicable to the point of atmospheric emission. If possible, stacks smaller than one foot in diameter should not be sampled.

8.1.1 Ideal Sampling Site. The ideal sampling site is at least eight stack or duct diameters downstream and two diameters upstream from any flow disturbance such as a bend, expansion or contraction. For rectangular cross sections, use Equation 103-1 in Section 12.2 to determine an equivalent diameter,  $D_e$ .

8.1.2 Alternate Sampling Site. Some sampling situations may render the above sampling site criteria impractical. In such cases, select an alternate site no less than two diameters downstream and one-half diameter upstream from any point of flow disturbance. Additional sample runs are recommended at any sample site not meeting the criteria of Section 8.1.1.

8.1.3 Number of Sample Runs Per Test. Three sample runs constitute a test. Conduct each run at one of three different points. Select three points that proportionately divide the diameter, or are located at 25, 50, and 75 percent of the diameter from the inside wall. For horizontal ducts, sample on a vertical line through the centroid. For rectangular ducts, sample on a line

through the centroid and parallel to a side. If additional sample runs are performed per Section 8.1.2, proportionately divide the duct to accommodate the total number of runs.

8.2 Measurement of Stack Conditions. Using the equipment described in Section 6.2, measure the stack gas pressure, moisture, and temperature to determine the molecular weight of the stack gas. Sound engineering estimates may be made in lieu of direct measurements. Describe the basis for such estimates in the test report.

8.3 Preparation of Sampling Train.

8.3.1 Assemble the sampling train as shown in Figure 103-1. It is recommended that all glassware be precleaned by soaking in wash acid for two hours.

8.3.2 Leak check the sampling train at the sampling site. The leakage rate should not be in excess of 1 percent of the desired sample rate.

8.4 Sampling Train Operation.

8.4.1 For each run, measure the velocity at the selected sampling point. Determine the isokinetic sampling rate. Record the velocity head and the required sampling rate. Place the nozzle at the sampling point with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. At the conclusion of the test, record the sampling rate. Again measure the velocity head at the sampling point. The required isokinetic rate at the end of the period should not have deviated more than 20 percent from that originally calculated. Describe the reason for any deviation beyond 20 percent in the test report.

8.4.2 Sample at a minimum rate of 14 liters/min (0.5 cfm). Obtain samples over such a period or periods of time as are necessary to determine the maximum emissions which would occur in a 24-hour period. In the case of cyclic operations, perform sufficient sample runs so as to allow determination or calculation of the emissions that occur over the duration of the cycle. A minimum sampling time of two hours per run is recommended.

8.5 Sample Recovery.

8.5.1 It is recommended that all glassware be precleaned as in Section 8.3. Sample recovery should also be performed in an area free of possible Be contamination. When the sampling train is moved, exercise care to prevent breakage and contamination. Set aside a portion of the acetone used in the sample recovery as a blank for analysis. The total amount of acetone used should be measured for accurate blank correction. Blanks can be eliminated if

prior analysis shows negligible amounts.

8.5.2 Remove the filter (and backup filter, if used) and any loose particulate matter from filter holder, and place in a container.

8.5.3 Clean the probe with acetone and a brush or long rod and cotton balls. Wash into the container with the filter. Wash out the filter holder with acetone, and add to the same container.

9.0 *Quality Control. [Reserved]*

10.0 *Calibration and Standardization*

10.1 *Sampling Train.* As a procedural check, compare the sampling rate regulation with a dry gas meter,

spirometer, rotameter (calibrated for prevailing atmospheric conditions), or equivalent, attached to the nozzle inlet of the complete sampling train.

10.2 *Analysis.* Perform the analysis standardization as suggested by the manufacturer of the instrument, or the procedures for the analytical method in use.

11.0 *Analytical Procedure*

Make the necessary preparation of samples and analyze for Be. Any currently acceptable method (e.g., atomic absorption, spectrographic, fluorometric, chromatographic) may be used.

12.0 *Data Analysis and Calculations*

12.1 *Nomenclature.*

$A_s(\text{avg})$  = Stack area,  $\text{m}^2$  ( $\text{ft}^2$ ).

$L$  = Length.

$R$  = Be emission rate, g/day.

$V_s(\text{avg})$  = Average stack gas velocity,  $\text{m}/\text{sec}$  ( $\text{ft}/\text{sec}$ ).

$V_{\text{total}}$  = Total volume of gas sampled,  $\text{m}^3$  ( $\text{ft}^3$ ).

$W$  = Width.

$W_t$  = Total weight of Be collected, mg.

$10^{-6}$  = Conversion factor, g/ $\mu\text{g}$ .

86,400 = Conversion factor, sec/day.

12.2 Calculate the equivalent diameter,  $D_e$ , for a rectangular cross section as follows:

$$D_e = \frac{2 \cdot L \cdot W}{L + W} \quad \text{Eq. 103-1}$$

12.3 Calculate the Be emission rate,  $R$ , in g/day for each stack using Equation 103-2. For cyclic operations,

use only the time per day each stack is in operation. The total Be emission rate

from a source is the summation of results from all stacks.

$$R = \frac{W_t V_{s(\text{avg})} A_s (86,400) (10^{-6})}{V_{\text{total}}} \quad \text{Eq. 103-2}$$

12.4 *Test Report.* Prepare a test report that includes as a minimum: A detailed description of the sampling train used, results of the procedural check described in Section 10.1 with all data and calculations made, all pertinent data taken during the test, the basis for any estimates made, isokinetic sampling calculations, and emission results. Include a description of the test site, with a block diagram and brief description of the process, location of the sample points in the stack cross section, and stack dimensions and distances from any point of disturbance.

13.0 *Method Performance. [Reserved]*

14.0 *Pollution Prevention. [Reserved]*

15.0 *Waste Management. [Reserved]*

16.0 *References. [Reserved]*

## 17.0 Tables, Diagrams, Flow Charts, and Validation Data

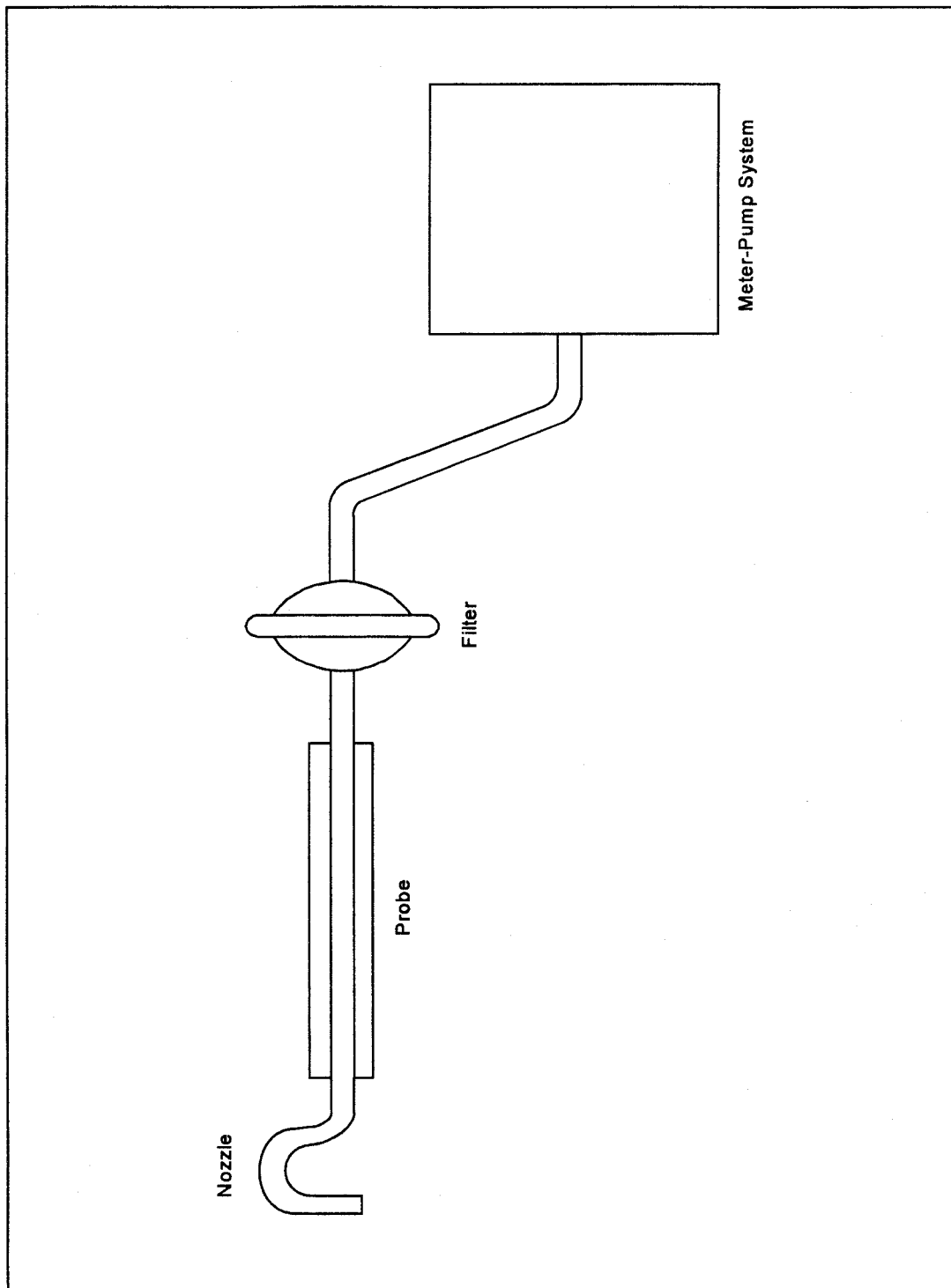


Figure 103-1. Beryllium Screening Method Sampling Train Schematic.

**Method 104—Determination of Beryllium Emissions From Stationary Sources**

**Note:** This method does not include all of the specifications (e.g., equipment and

supplies) and procedures (e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from methods in Appendix A to 40 CFR part 60. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following

additional test methods: Method 1, Method 2, Method 3, and Method 5 in Appendix A, Part 60.

**1.0 Scope and Application****1.1 Analytes.**

Analyte	CAS No.	Sensitivity
Beryllium (Be) .....	7440-41-7	Dependent upon recorder and spectrophotometer.

1.2 Applicability. This method is applicable for the determination of Be emissions in ducts or stacks at stationary sources. Unless otherwise specified, this method is not intended to apply to gas streams other than those emitted directly to the atmosphere without further processing.

1.3 Data Quality Objectives. Adherences to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

**2.0 Summary of Method**

2.1 Particulate and gaseous Be emissions are withdrawn isokinetically from the source and are collected on a glass fiber filter and in water. The collected sample is digested in an acid solution and is analyzed by atomic absorption spectrophotometry.

**3.0 Definitions [Reserved]****4.0 Interferences**

4.1 Matrix Effects. Analysis for Be by flame atomic absorption spectrophotometry is sensitive to the chemical composition and to the physical properties (e.g., viscosity, pH) of the sample. Aluminum and silicon in particular are known to interfere when present in appreciable quantities. The analytical procedure includes (optionally) the use of the Method of Standard Additions to check for these matrix effects, and sample analysis using the Method of Standard Additions if significant matrix effects are found to be present (see Reference 2 in Section 16.0).

**5.0 Safety**

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe

procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burn as thermal burn.

5.2.1 Hydrochloric Acid (HCl). Highly toxic. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or edema of lungs. Exposure to concentrations of 0.13 to 0.2 percent can be lethal to humans in a few minutes. Provide ventilation to limit exposure. Reacts with metals, producing hydrogen gas.

5.2.2 Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>). Irritating to eyes, skin, nose, and lungs.

5.2.3 Nitric Acid (HNO<sub>3</sub>). Highly corrosive to eyes, skin, nose, and lungs. Vapors cause bronchitis, pneumonia, or edema of lungs. Reaction to inhalation may be delayed as long as 30 hours and still be fatal. Provide ventilation to limit exposure. Strong oxidizer. Hazardous reaction may occur with organic materials such as solvents.

5.2.4 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.3 Beryllium is hazardous, and precautions should be taken to minimize exposure.

**6.0 Equipment and Supplies**

6.1 Sample Collection. Same as Method 5, Section 6.1, with the exception of the following:

6.1.1 Sampling Train. Same as Method 5, Section 6.1.1, with the exception of the following:

6.1.2 Probe Liner. Borosilicate or quartz glass tubing. A heating system capable of maintaining a gas temperature of 120 ± 14 °C (248 ± 25 °F) at the probe exit during sampling to prevent water condensation may be used.

**Note:** Do not use metal probe liners.

6.1.3 Filter Holder. Borosilicate glass, with a glass frit filter support and a silicone rubber gasket. Other materials of construction (e.g., stainless steel,

Teflon, Viton) may be used, subject to the approval of the Administrator. The holder design shall provide a positive seal against leakage from the outside or around the filter. The holder shall be attached immediately at the outlet of the probe. A heating system capable of maintaining the filter at a minimum temperature in the range of the stack temperature may be used to prevent condensation from occurring.

6.1.4 Impingers. Four Greenburg-Smith impingers connected in series with leak-free ground glass fittings or any similar leak-free noncontaminating fittings. For the first, third, and fourth impingers, use impingers that are modified by replacing the tip with a 13 mm-ID (0.5 in.) glass tube extending to 13 mm (0.5 in.) from the bottom of the flask may be used.

6.2 Sample Recovery. The following items are needed for sample recovery:

6.2.1 Probe Cleaning Rod. At least as long as probe.

6.2.2 Glass Sample Bottles. Leakless, with Teflon-lined caps, 1000 ml.

6.2.3 Petri Dishes. For filter samples, glass or polyethylene, unless otherwise specified by the Administrator.

6.2.4 Graduated Cylinder. 250 ml.

6.2.5 Funnel and Rubber Policeman. To aid in transfer of silica gel to container; not necessary if silica gel is weighed in the field.

6.2.6 Funnel. Glass, to aid in sample recovery.

6.2.7 Plastic Jar. Approximately 300 ml.

6.3 Analysis. The following items are needed for sample analysis:

6.3.1 Atomic Absorption Spectrophotometer. Perkin-Elmer 303, or equivalent, with nitrous oxide/acetylene burner.

6.3.2 Hot Plate.

6.3.3 Perchloric Acid Fume Hood.

**7.0 Reagents and Standards**

**Note:** Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Collection. Same as Method 5, Section 7.1, including deionized distilled water conforming to ASTM D 1193-77 or 91 (incorporated by reference—see § 61.18), Type 3. The Millipore AA filter is recommended.

7.2 Sample Recovery. Same as Method 5 in Appendix A, Part 60, Section 7.2, with the addition of the following:

7.2.1 Wash Acid, 50 Percent (V/V) Hydrochloric Acid (HCl). Mix equal volumes of concentrated HCl and water, being careful to add the acid slowly to the water.

7.3 Sample Preparation and Analysis. The following reagents and standards and standards are needed for sample preparation and analysis:

7.3.1 Water. Same as in Section 7.1.

7.3.2 Perchloric Acid (HClO<sub>4</sub>). Concentrated (70 percent V/V).

7.3.3 Nitric Acid (HNO<sub>3</sub>). Concentrated.

7.3.4 Beryllium Powder. Minimum purity 98 percent.

7.3.5 Sulfuric Acid (H<sub>2</sub>SO<sub>4</sub>) Solution, 12 N. Dilute 33 ml of concentrated H<sub>2</sub>SO<sub>4</sub> to 1 liter with water.

7.3.6 Hydrochloric Acid Solution, 25 Percent HCl (V/V).

7.3.7 Stock Beryllium Standard Solution, 10 µg Be/ml. Dissolve 10.0 mg of Be in 80 ml of 12 N H<sub>2</sub>SO<sub>4</sub> in a 1000-ml volumetric flask. Dilute to volume with water. This solution is stable for at least one month. Equivalent strength Be stock solutions may be prepared from Be salts such as BeCl<sub>2</sub> and Be(NO<sub>3</sub>)<sub>2</sub> (98 percent minimum purity).

7.3.8 Working Beryllium Standard Solution, 1 µg Be/ml. Dilute a 10 ml aliquot of the stock beryllium standard solution to 100 ml with 25 percent HCl solution to give a concentration of 1 mg/ml. Prepare this dilute stock solution fresh daily.

#### 8.0 Sample Collection, Preservation, Transport, and Storage

The amount of Be that is collected is generally small, therefore, it is necessary to exercise particular care to prevent contamination or loss of sample.

8.1 Pretest Preparation. Same as Method 5, Section 8.1, except omit Section 8.1.3.

8.2 Preliminary Determinations. Same as Method 5, Section 8.2, with the exception of the following:

8.2.1 Select a nozzle size based on the range of velocity heads to assure that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates below 28 liters/min (1.0 cfm).

8.2.2 Obtain samples over a period or periods of time that accurately determine the maximum emissions that occur in a 24-hour period. In the case of cyclic operations, perform sufficient sample runs for the accurate determination of the emissions that occur over the duration of the cycle. A minimum sample time of 2 hours per run is recommended.

8.3 Preparation of Sampling Train. Same as Method 5, Section 8.3, with the exception of the following:

8.3.1 Prior to assembly, clean all glassware (probe, impingers, and connectors) by first soaking in wash acid for 2 hours, followed by rinsing with water.

8.3.2 Save a portion of the water for a blank analysis.

8.3.3 Procedures relating to the use of metal probe liners are not applicable.

8.3.4 Probe and filter heating systems are needed only if water condensation is a problem. If this is the case, adjust the heaters to provide a temperature at or above the stack temperature. However, membrane filters such as the Millipore AA are limited to about 107 °C (225 °F). If the stack gas is in excess of about 93 °C (200 °F), consideration should be given to an alternate procedure such as moving the filter holder downstream of the first impinger to insure that the filter does not exceed its temperature limit. After the sampling train has been assembled, turn on and set the probe heating system, if applicable, at the desired operating temperature. Allow time for the temperatures to stabilize. Place crushed ice around the impingers.

**Note:** An empty impinger may be inserted between the third impinger and the silica gel to remove excess moisture from the sample stream.

8.4 Leak Check Procedures, Sampling Train Operation, and

Calculation of Percent Isokinetic. Same as Method 5, Sections 8.4, 8.5, and 8.6, respectively.

8.5 Sample Recovery. Same as Method 5, Section 8.7, except treat the sample as follows: Transfer the probe and impinger assembly to a cleanup area that is clean, protected from the wind, and free of Be contamination. Inspect the train before and during this assembly, and note any abnormal conditions. Treat the sample as follows: Disconnect the probe from the impinger train.

8.5.1 Container No. 1. Same as Method 5, Section 8.7.6.1.

8.5.2 Container No. 2. Place the contents (measured to 1 ml) of the first three impingers into a glass sample bottle. Use the procedures outlined in Section 8.7.6.2 of Method 5, where applicable, to rinse the probe nozzle, probe fitting, probe liner, filter holder, and all glassware between the filter holder and the back half of the third impinger with water. Repeat this procedure with acetone. Place both water and acetone rinse solutions in the sample bottle with the contents of the impingers.

8.5.3 Container No. 3. Same as Method 5, Section 8.7.6.3.

#### 8.6 Blanks.

8.6.1 Water Blank. Save a portion of the water as a blank. Take 200 ml directly from the wash bottle being used and place it in a plastic sample container labeled "H<sub>2</sub>O blank."

8.6.2 Filter. Save two filters from each lot of filters used in sampling. Place these filters in a container labeled "filter blank."

8.7 Post-test Glassware Rinsing. If an additional test is desired, the glassware can be carefully double rinsed with water and reassembled. However, if the glassware is out of use more than 2 days, repeat the initial acid wash procedure.

#### 9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.4, 10.1 .....	Sampling equipment leak checks and calibration .....	Ensure accuracy and precision of sampling measurements.
10.2 .....	Spectrophotometer calibration .....	Ensure linearity of spectrophotometer response to standards.
11.5 .....	Check for matrix effects .....	Eliminate matrix effects.
11.6 .....	Audit sample analysis .....	Evaluate analyst's technique and standards preparation.

9.2 Volume Metering System Checks. Same as Method 5, Section 9.2.

## 10.0 Calibration and Standardization

**Note:** Maintain a laboratory log of all calibrations.

10.1 Sampling Equipment. Same as Method 5, Section 10.0.

10.2 Preparation of Standard Solutions. Pipet 1, 3, 5, 8, and 10 ml of the 1.0 µg Be/ml working standard solution into separate 100 ml volumetric flasks, and dilute to the mark with water. The total amounts of Be in these standards are 1, 3, 5, 8, and 10 µg, respectively.

10.3 Spectrophotometer and Recorder. The Be response may be measured by either peak height or peak area. Analyze an aliquot of the 10-µg standard at 234.8 nm using a nitrous oxide/acetylene flame. Determine the maximum absorbance of the standard, and set this value to read 90 percent of the recorder full scale.

### 10.4 Calibration Curve.

10.4.1 After setting the recorder scale, analyze an appropriately sized aliquot of each standard and the BLANK (see Section 11) until two consecutive peaks agree within 3 percent of their average value.

10.4.3 Subtract the average peak height (or peak area) of the blank—which must be less than 2 percent of recorder full scale—from the averaged peak heights of the standards. If the blank absorbance is greater than 2 percent of full-scale, the probable cause is Be contamination of a reagent or carry-over of Be from a previous sample. Prepare the calibration curve by plotting the corrected peak height of each standard solution versus the corresponding total Be weight in the standard (in µg).

10.5 Spectrophotometer Calibration Quality Control. Calculate the least squares slope of the calibration curve. The line must pass through the origin or through a point no further from the origin than ±2 percent of the recorder full scale. Multiply the corrected peak height by the reciprocal of the least squares slope to determine the distance each calibration point lies from the theoretical calibration line. The difference between the calculated concentration values and the actual concentrations (i.e., 1, 3, 5, 8, and 10 µg Be) must be less than 7 percent for all standards.

## 11.0 Analytical Procedure

11.1 Sample Loss Check. Prior to analysis, check the liquid level in Container No. 2. Note on the analytical data sheet whether leakage occurred during transport. If a noticeable amount

of leakage occurred, either void the sample or take steps, subject to the approval of the Administrator, to adjust the final results.

11.2 Glassware Cleaning. Before use, clean all glassware according to the procedure of Section 8.3.1.

11.3 Sample Preparation. The digestion of Be samples is accomplished in part in concentrated HClO<sub>4</sub>.

**Note:** The sample must be heated to light brown fumes after the initial HNO<sub>3</sub> addition; otherwise, dangerous perchlorates may result from the subsequent HClO<sub>4</sub> digestion. HClO<sub>4</sub> should be used only under a hood.

11.3.1 Container No. 1. Transfer the filter and any loose particulate matter from Container No. 1 to a 150-ml beaker. Add 35 ml concentrated HNO<sub>3</sub>. To oxidize all organic matter, heat on a hotplate until light brown fumes are evident. Cool to room temperature, and add 5 ml 12 N H<sub>2</sub>SO<sub>4</sub> and 5 ml concentrated HClO<sub>4</sub>.

11.3.2 Container No. 2. Place a portion of the water and acetone sample into a 150 ml beaker, and put on a hotplate. Add portions of the remainder as evaporation proceeds and evaporate to dryness. Cool the residue, and add 35 ml concentrated HNO<sub>3</sub>. To oxidize all organic matter, heat on a hotplate until light brown fumes are evident. Cool to room temperature, and add 5 ml 12 N H<sub>2</sub>SO<sub>4</sub> and 5 ml concentrated HClO<sub>4</sub>. Then proceed with step 11.3.4.

11.3.3 Final Sample Preparation. Add the sample from Section 11.3.2 to the 150-ml beaker from Section 11.3.1. Replace on a hotplate, and evaporate to dryness in a HClO<sub>4</sub> hood. Cool the residue to room temperature, add 10.0 ml of 25 percent V/V HCl, and mix to dissolve the residue.

11.3.4 Filter and Water Blanks. Cut each filter into strips, and treat each filter individually as directed in Section 11.3.1. Treat the 200-ml water blank as directed in Section 11.3.2. Combine and treat these blanks as directed in Section 11.3.3.

11.4 Spectrophotometer Preparation. Turn on the power; set the wavelength, slit width, and lamp current; and adjust the background corrector as instructed by the manufacturer's manual for the particular atomic absorption spectrophotometer. Adjust the burner and flame characteristics as necessary.

11.5 Analysis. Calibrate the analytical equipment and develop a calibration curve as outlined in Sections 10.4 and 10.5.

11.5.1 Beryllium Samples. Repeat the procedure used to establish the calibration curve with an appropriately sized aliquot of each sample (from Section 11.3.3) until two consecutive peak heights agree within 3 percent of

their average value. The peak height of each sample must be greater than 10 percent of the recorder full scale. If the peak height of the sample is off scale on the recorder, further dilute the original source sample to bring the Be concentration into the calibration range of the spectrophotometer.

11.5.2 Run a blank and standard at least after every five samples to check the spectrophotometer calibration. The peak height of the blank must pass through a point no further from the origin than ±2 percent of the recorder full scale. The difference between the measured concentration of the standard (the product of the corrected peak height and the reciprocal of the least squares slope) and the actual concentration of the standard must be less than 7 percent, or recalibration of the analyzer is required.

11.5.3 Check for Matrix Effects (optional). Use the Method of Standard Additions (see Reference 2 in Section 16.0) to check at least one sample from each source for matrix effects on the Be results. If the results of the Method of Standard Additions procedure used on the single source sample do not agree to within 5 percent of the value obtained by the routine atomic absorption analysis, then reanalyze all samples from the source using the Method of Standard Additions procedure.

11.6 Container No. 2 (Silica Gel). Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance. (This step may be conducted in the field.)

## 12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra decimal significant figure beyond that of the acquired data. Round off figures only after the final calculation. Other forms of the equations may be used as long as they give equivalent results.

### 12.1 Nomenclature.

$K_1 = 0.3858$  °K/mm Hg for metric units.

$= 17.64$  °R/in. Hg for English units.

$K_3 = 10^{-6}$  g/µg for metric units.

$= 2.2046 \times 10^{-9}$  lb/µg for English units.

$m_{Be}$  = Total weight of beryllium in the source sample.

$P_s$  = Absolute stack gas pressure, mm Hg (in. Hg).

$t$  = Daily operating time, sec/day.

$T_s$  = Absolute average stack gas temperature, °K (°R).

$V_{m(std)}$  = Dry gas sample volume at standard conditions, scm (scf).

$V_{w(std)}$  = Volume of water vapor at standard conditions, scm (scf).

12.2 Average Dry Gas Meter Temperature and Average Orifice

Pressure Drop, Dry Gas Volume, Volume of Water Vapor Condensed, Moisture Content, Isokinetic Variation, and Stack Gas Velocity and Volumetric Flow Rate. Same as Method 5, Sections 12.2 through 12.5, 12.11, and 12.12, respectively.

12.3 Total Beryllium. For each source sample, correct the average maximum absorbance of the two

consecutive samples whose peak heights agree within 3 percent of their average for the contribution of the solution blank (see Sections 11.3.4 and 11.5.2). Correcting for any dilutions if necessary, use the calibration curve and these corrected averages to determine the total weight of Be in each source sample.

$$R = \frac{K_1 K_3 t m_{Be} P_s v_s A_s}{T_s (V_{m(std)} + V_{w(std)})} \quad \text{Eq. 104-1}$$

12.5 Determination of Compliance. Each performance test consists of three sample runs. For the purpose of determining compliance with an applicable national emission standard, use the average of the results of all sample runs.

13.0 Method Performance. [Reserved]

14.0 Pollution Prevention. [Reserved]

15.0 Waste Management. [Reserved]

16.0 References

Same as References 1, 2, and 4–11 of Section 16.0 of Method 101 with the addition of the following:

1. Amos, M.D., and J.B. Willis. Use of High-Temperature Pre-Mixed Flames in Atomic Absorption Spectroscopy. *Spectrochim. Acta*. 22:1325. 1966.

2. Fleet, B., K.V. Liberty, and T. S. West. A Study of Some Matrix Effects in the Determination of Beryllium by Atomic Absorption Spectroscopy in the Nitrous Oxide-Acetylene Flame. *Talanta* 17:203. 1970.

17.0 Tables, Diagrams, Flowcharts, And Validation Data [Reserved]

#### Method 105—Determination of Mercury in Wastewater Treatment Plant Sewage Sludges

**Note:** This method does not include all of the specifications (e.g., equipment and

12.4 Beryllium Emission Rate. Calculate the daily Hg emission rate, R, using Equation 104–1. For continuous operations, the operating time is equal to 86,400 seconds per day. For cyclic operations, use only the time per day each stack is in operation. The total Hg emission rate from a source will be the summation of results from all stacks.

supplies) and procedures (e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should also have a thorough knowledge of at least the following additional test methods: Method 101 and Method 101A.

#### 1.0 Scope and Application

##### 1.1 Analytes.

Analyte	CAS No.	Sensitivity
Mercury (Hg) .....	7439–97–6	Dependent upon spectrophotometer and recorder.

1.2 Applicability. This method is applicable for the determination of total organic and inorganic Hg content in sewage sludges.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

#### 2.0 Summary of Method

2.1 Time-composite sludge samples are withdrawn from the conveyor belt subsequent to dewatering and before incineration or drying. A weighed portion of the sludge is digested in aqua regia and is oxidized by potassium permanganate (KMnO<sub>4</sub>). Mercury in the digested sample is then measured by the conventional spectrophotometric cold-vapor technique.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

#### 5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations,

and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burn as thermal burn.

5.2.1 Hydrochloric Acid (HCl). Highly toxic. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or edema of lungs. Exposure to concentrations of 0.13 to 0.2 percent can be lethal to humans in a few minutes. Provide ventilation to limit exposure. Reacts with metals, producing hydrogen gas.

5.2.2 Nitric Acid (HNO<sub>3</sub>). Highly corrosive to eyes, skin, nose, and lungs. Vapors cause bronchitis, pneumonia, or edema of lungs. Reaction to inhalation may be delayed as long as 30 hours and still be fatal. Provide ventilation to limit exposure. Strong oxidizer. Hazardous reaction may occur with organic materials such as solvents.

#### 6.0 Equipment and Supplies

6.1 Sample Collection and Mixing. The following items are required for collection and mixing of the sludge samples:

6.1.1 Container. Plastic, 50-liter.

6.1.2 Scoop. To remove 950-ml (1 quart.) sludge sample.

6.1.3 Mixer. Mortar mixer, wheelbarrow-type, 57-liter (or equivalent) with electricity-driven motor.

6.1.4 Blender. Waring-type, 2-liter.

6.1.5 Scoop. To remove 100-ml and 20-ml samples of blended sludge.

6.1.6 Erlenmeyer Flasks. Four, 125-ml.

6.1.7 Beakers. Glass beakers in the following sizes: 50 ml (1), 200 ml (1), 400 ml (2).

6.2 Sample Preparation and Analysis. Same as Method 101, Section 6.3, with the addition of the following:

6.2.1 Hot Plate.

6.2.2 Desiccator.

6.2.3 Filter Paper. S and S No. 588 (or equivalent).

6.2.4 Beakers. Glass beakers, 200 ml and 400 ml (2 each).

#### 7.0 Reagents and Standards

**Note:** Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Analysis. Same as Method 101A, Section 7.2, with the following additions and exceptions:

7.1.1 Hydrochloric Acid. The concentrated HCl specified in Method 101A, Section 7.2.4, is not required.

7.1.2 Aqua Regia. Prepare immediately before use. Carefully add one volume of concentrated HNO<sub>3</sub> to three volumes of concentrated HCl.

#### 8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sludge Sampling. Withdraw equal volume increments of sludge [for a total of at least 15 liters (16 quarts)] at intervals of 30 min over an 8-hr period, and combine in a rigid plastic container.

8.2 Sludge Mixing. Transfer the entire 15-liter sample to a mortar mixer. Mix the sample for a minimum of 30 min at 30 rpm. Take six 100-ml portions of sludge, and combine in a 2-liter blender. Blend sludge for 5 min; add water as necessary to give a fluid consistency. Immediately after stopping the blender, withdraw four 20-ml portions of blended sludge, and place them in separate, tared 125-ml Erlenmeyer flasks. Reweigh each flask to determine the exact amount of sludge added.

8.3 Sample Holding Time. Samples shall be analyzed within the time specified in the applicable subpart of the regulations.

#### 9.0 Quality Control

Section	Quality control measure	Effect
10.0 .....	Spectrophotometer calibration .....	Ensure linearity of spectrophotometer response to standards.
11.0 .....	Check for matrix effects .....	Eliminate matrix effects.

#### 10.0 Calibration and Standardization

Same as Method 101A, Section 10.2.

#### 11.0 Analytical Procedures

11.1 Solids Content of Blended Sludge. Dry one of the 20-ml blended samples from Section 8.2 in an oven at 105 °C (221 °F) to constant weight. Cool in a desiccator, weigh and record the dry weight of the sample.

11.2 Aqua Regia Digestion of Blended Samples.

11.2.1 To each of the three remaining 20-ml samples from Section 8.2 add 25 ml of aqua regia, and digest the on a hot plate at low heat (do not boil) for 30 min, or until samples are a pale yellow-brown color and are void of the dark brown color characteristic of organic matter. Remove from hotplate and allow to cool.

11.2.2 Filter each digested sample separately through an S and S No. 588 filter or equivalent, and rinse the filter contents with 50 ml of water. Transfer the filtrate and filter washing to a 100-ml volumetric flask, and carefully dilute to volume with water.

11.3 Solids Content of the Sludge Before Blending. Remove two 100-ml

portions of mixed sludge from the mortar mixer and place in separate, tared 400-ml beakers. Reweigh each beaker to determine the exact amount of sludge added. Dry in oven at 105 °C (221 °F) and cool in a desiccator to constant weight.

11.4 Analysis for Mercury. Analyze the three aqua regia-digested samples using the procedures outlined in Method 101A, Section 11.0.

#### 12.0 Data Analysis and Calculations

12.1 Nomenclature.

C<sub>m</sub> = Concentration of Hg in the digested sample, µg/g.

F<sub>sb</sub> = Weight fraction of solids in the blended sludge.

F<sub>sm</sub> = Weight fraction of solids in the collected sludge after mixing.

M = Hg content of the sewage sludge (on a dry basis), µg/g.

m = Mass of Hg in the aliquot of digested sample analyzed, µg.

n = number of digested samples (specified in Section 11.2 as three).

V<sub>a</sub> = Volume of digested sample analyzed, ml.

V<sub>s</sub> = Volume of digested sample, ml.

W<sub>b</sub> = Weight of empty sample beaker, g.

W<sub>bs</sub> = Weight of sample beaker and sample, g.

W<sub>bd</sub> = Weight of sample beaker and sample after drying, g.

W<sub>f</sub> = Weight of empty sample flask, g.

W<sub>fd</sub> = Weight of sample flask and sample after drying, g.

W<sub>fs</sub> = Weight of sample flask and sample, g.

12.2 Mercury Content of Digested Sample (Wet Basis).

12.2.1 For each sample analyzed for Hg content, calculate the arithmetic mean maximum absorbance of the two consecutive samples whose peak heights agree ±3 percent of their average. Correct this average value for the contribution of the blank. Use the calibration curve and these corrected averages to determine the final Hg concentration in the solution cell for each sludge sample.

12.2.2 Calculate the average Hg concentration of the digested samples by correcting for any dilutions made to bring the sample into the working range of the spectrophotometer and for the weight of the sludge portion digested, using Equation 105-1.

$$\bar{C}_m = \sum_{i=1}^n \left[ \frac{mV_s}{V_a(W_{fs} - W_f)} \right]_i \quad \text{Eq. 105-1}$$

12.3 Solids Content of Blended Sludge. Determine the solids content of

the blended sludge using Equation 105-2.

$$F_{sb} = 1 - \frac{W_{fs} - W_{fd}}{W_{fs} - W_f}$$
 Eq. 105-2

12.4 Solids Content of Bulk Sample (before blending but, after mixing in mortar mixer). Determine the solids content of each 100 ml aliquot (Section 11.3), and average the results.

$$F_{sm} = 1 - \frac{W_{bs} - W_{bd}}{W_{bs} - W_b}$$
 Eq. 105-3

12.5 Mercury Content of Bulk Sample (Dry Basis). Average the results from the three samples from each 8-hr composite sample, and calculate the Hg concentration of the composite sample on a dry basis.

$$M = \frac{\bar{C}_m}{F_{sb}}$$
 Eq. 105-4

13.0 Method Performance

13.1 Range. The range of this method is 0.2 to 5 micrograms per gram; it may be extended by increasing or decreasing sample size.

14.0 Pollution Prevention. [Reserved]

15.0 Waste Management. [Reserved]

16.0 References

1. Bishop, J.N. Mercury in Sediments. Ontario Water Resources Commission. Toronto, Ontario, Canada. 1971.  
2. Salma, M. Private Communication. EPA California/Nevada Basin Office. Alameda, California.  
3. Hatch, W.R. and W.L. Ott. Determination of Sub-Microgram Quantities of Mercury by

Atomic Absorption Spectrophotometry. Analytical Chemistry. 40:2085. 1968.  
4. Bradenberger, H., and H. Bader. The Determination of Nanogram Levels of Mercury in Solution by a Flameless Atomic Absorption Technique. Atomic Absorption Newsletter. 6:101. 1967.  
5. Analytical Quality Control Laboratory (AQCL). Mercury in Sediment (Cold Vapor Technique) (Provisional Method). U.S. Environmental Protection Agency. Cincinnati, Ohio. April 1972.  
6. Kopp, J.F., M.C. Longbottom, and L.B. Lobring. "Cold Vapor" Method for Determining Mercury. Journal AWWA. 64(1):20-25. 1972.  
7. Manual of Methods for Chemical Analysis of Water and Wastes. U.S. Environmental Protection Agency. Cincinnati, Ohio. Publication No. EPA-624/2-74-003. December 1974. pp. 118-138.  
8. Mitchell, W.J., M.R. Midgett, J. Suggs, R.J. Velton, and D. Albrink. Sampling and Homogenizing Sewage for Analysis. Environmental Monitoring and Support Laboratory, Office of Research and Development, U.S. Environmental Protection Agency. Research Triangle Park, N.C. March 1979. p. 7.  
17.0 Tables, Diagrams, Flowcharts, and Validation Data. [Reserved]  
**Method 106—Determination of Vinyl Chloride Emissions From Stationary Sources**  
1.0 Scope and Application  
1.1 Analytes.

Analyte	CAS No.	Sensitivity
Vinyl Chloride (CH <sub>2</sub> :CHCl) .....	75-01-4	Dependent upon analytical equipment.

1.2 Applicability. This method is applicable for the determination of vinyl chloride emissions from ethylene dichloride, vinyl chloride, and polyvinyl chloride manufacturing processes. This method does not measure vinyl chloride contained in particulate matter.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 An integrated bag sample of stack gas containing vinyl chloride is subjected to GC analysis using a flame ionization detector (FID).

3.0 Definitions. [Reserved]

4.0 Interferences

4.1 Resolution interferences of vinyl chloride may be encountered on some sources. Therefore, the chromatograph operator should select the column and operating parameters best suited to the particular analysis requirements. The selection made is subject to approval of the Administrator. Approval is automatic, provided that confirming data are produced through an adequate supplemental analytical technique, and that the data are available for review by the Administrator. An example of this would be analysis with a different column or GC/mass spectroscopy.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations,

and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Toxic Analyte. Care must be exercised to prevent exposure of sampling personnel to vinyl chloride, which is a carcinogen.

6.0 Equipment and Supplies

6.1 Sample Collection (see Figure 106-1). The sampling train consists of the following components:

6.1.1 Probe. Stainless steel, borosilicate glass, Teflon tubing (as stack temperature permits), or equivalent, equipped with a glass wool plug to remove particulate matter.

6.1.2 Sample Lines. Teflon, 6.4-mm outside diameter, of sufficient length to connect probe to bag. Use a new unused piece for each series of bag samples that constitutes an emission test, and discard upon completion of the test.

6.1.3 Quick Connects. Stainless steel, male (2) and female (2), with ball checks (one pair without), located as shown in Figure 106-1.

6.1.4 Tedlar Bags. 50- to 100-liter capacity, to contain sample. Aluminized Mylar bags may be used if the samples are analyzed within 24 hours of collection.

6.1.5 Bag Containers. Rigid leak-proof containers for sample bags, with covering to protect contents from sunlight.

6.1.6 Needle Valve. To adjust sample flow rates.

6.1.7 Pump. Leak-free, with minimum of 2-liter/min capacity.

6.1.8 Charcoal Tube. To prevent admission of vinyl chloride and other organics to the atmosphere in the vicinity of samplers.

6.1.9 Flowmeter. For observing sampling flow rate; capable of measuring a flow range from 0.10 to 1.00 liter/min.

6.1.10 Connecting Tubing. Teflon, 6.4-mm outside diameter, to assemble sampling train (Figure 106-1).

6.1.11 Tubing Fittings and Connectors. Teflon or stainless steel, to assemble sampling training.

6.2 Sample Recovery. Teflon tubing, 6.4-mm outside diameter, to connect bag to GC sample loop. Use a new unused piece for each series of bag samples that constitutes an emission test, and discard upon conclusion of analysis of those bags.

6.3 Analysis. The following equipment is required:

6.3.1 Gas Chromatograph. With FID potentiometric strip chart recorder and 1.0 to 5.0-ml heated sampling loop in automatic sample valve. The chromatographic system shall be capable of producing a response to 0.1-ppmv vinyl chloride that is at least as great as the average noise level. (Response is measured from the average value of the base line to the maximum of the wave form, while standard operating conditions are in use.)

6.3.2 Chromatographic Columns. Columns as listed below. Other columns may be used provided that the precision and accuracy of the analysis of vinyl chloride standards are not impaired and that information is available for review confirming that there is adequate resolution of vinyl chloride peak. (Adequate resolution is defined as an area overlap of not more than 10 percent of the vinyl chloride peak by an

interferent peak. Calculation of area overlap is explained in Procedure 1 of appendix C to this part: "Determination of Adequate Chromatographic Peak Resolution.")

6.3.2.1 Column A. Stainless steel, 2.0 m by 3.2 mm, containing 80/100-mesh Chromasorb 102.

6.3.2.2 Column B. Stainless steel, 2.0 m by 3.2 mm, containing 20 percent GE SF-96 on 60/100-mesh Chromasorb P AW; or stainless steel, 1.0 m by 3.2 mm containing 80/100-mesh Porapak T. Column B is required as a secondary column if acetaldehyde is present. If used, column B is placed after column A. The combined columns should be operated at 120 °C (250 °F).

6.3.3 Rate Meters (2). Rotameter, or equivalent, 100-ml/min capacity, with flow control valves.

6.3.4 Gas Regulators. For required gas cylinders.

6.3.5 Temperature Sensor. Accurate to  $\pm 1$  °C ( $\pm 2$  °F), to measure temperature of heated sample loop at time of sample injection.

6.3.6 Barometer. Accurate to  $\pm 5$  mm Hg, to measure atmospheric pressure around GC during sample analysis.

6.3.7 Pump. Leak-free, with minimum of 100-ml/min capacity.

6.3.8 Recorder. Strip chart type, optionally equipped with either disc or electronic integrator.

6.3.9 Planimeter. Optional, in place of disc or electronic integrator on recorder, to measure chromatograph peak areas.

6.4 Calibration and Standardization.

6.4.1 Tubing. Teflon, 6.4-mm outside diameter, separate pieces marked for each calibration concentration.

**Note:** The following items are required only if the optional standard gas preparation procedures (Section 10.1) are followed.

6.4.2 Tedlar Bags. Sixteen-inch-square size, with valve; separate bag marked for each calibration concentration.

6.4.3 Syringes. 0.5-ml and 50- $\mu$ l, gas tight, individually calibrated to dispense gaseous vinyl chloride.

6.4.4 Dry Gas Meter with Temperature and Pressure Gauges. Singer Model DTM-115 with 802 index, or equivalent, to meter nitrogen in preparation of standard gas mixtures, calibrated at the flow rate used to prepare standards.

## 7.0 Reagents and Standards

7.1 Analysis. The following reagents are required for analysis.

7.1.1 Helium or Nitrogen. Purity 99.9995 percent or greater, for chromatographic carrier gas.

7.1.2 Hydrogen. Purity 99.9995 percent or greater.

7.1.3 Oxygen or Air. Either oxygen (purity 99.99 percent or greater) or air (less than 0.1 ppmv total hydrocarbon content), as required by detector.

7.2 Calibration. Use one of the following options: either Sections 7.2.1 and 7.2.2, or Section 7.2.3.

7.2.1 Vinyl Chloride. Pure vinyl chloride gas certified by the manufacturer to contain a minimum of 99.9 percent vinyl chloride. If the gas manufacturer maintains a bulk cylinder supply of 99.9+ percent vinyl chloride, the certification analysis may have been performed on this supply, rather than on each gas cylinder prepared from this bulk supply. The date of gas cylinder preparation and the certified analysis must have been affixed to the cylinder before shipment from the gas manufacturer to the buyer.

7.2.2 Nitrogen. Same as described in Section 7.1.1.

7.2.3 Cylinder Standards. Gas mixture standards (50-, 10-, and 5 ppmv vinyl chloride) in nitrogen cylinders may be used to directly prepare a chromatograph calibration curve as described in Section 10.3 if the following conditions are met: (a) The manufacturer certifies the gas composition with an accuracy of  $\pm 3$  percent or better. (b) The manufacturer recommends a maximum shelf life over which the gas concentration does not change by greater than  $\pm 5$  percent from the certified value. (c) The manufacturer affixes the date of gas cylinder preparation, certified vinyl chloride concentration, and recommended maximum shelf to the cylinder before shipment to the buyer.

7.2.3.1 Cylinder Standards Certification. The manufacturer shall certify the concentration of vinyl chloride in nitrogen in each cylinder by (a) directly analyzing each cylinder and (b) calibrating his analytical procedure on the day of cylinder analysis. To calibrate his analytical procedure, the manufacturer shall use as a minimum, a three point calibration curve. It is recommended that the manufacturer maintain (1) a high concentration calibration standard (between 50 and 100 ppmv) to prepare his calibration curve by an appropriate dilution technique and (2) a low-concentration calibration standard (between 5 and 10 ppmv) to verify the dilution technique used. If the difference between the apparent concentration read from the calibration curve and the true concentration assigned to the low-concentration calibration standard exceeds 5 percent of the true concentration, the manufacturer shall

determine the source of error and correct it, then repeat the three-point calibration.

7.2.3.2 Verification of Manufacturer's Calibration Standards. Before using a standard, the manufacturer shall verify each calibration standard (a) by comparing it to gas mixtures prepared (with 99 mole percent vinyl chloride) in accordance with the procedure described in Section 7.2.1 or (b) calibrating it against vinyl chloride cylinder Standard Reference Materials (SRM's) prepared by the National Institute of Standards and Technology, if such SRM's are available. The agreement between the initially determined concentration value and the verification concentration value must be ±5 percent. The manufacturer must reverify all calibration standards on a time interval consistent with the shelf life of the cylinder standards sold.

7.2.4 Audit Cylinder Standards.  
7.2.4.1 Gas mixture standards with concentrations known only to the person supervising the analysis of samples. The concentrations of the audit cylinders should be: one low-concentration cylinder in the range of 5 to 20 ppmv vinyl chloride and one high-concentration cylinder in the range of 20 to 50 ppmv. When available, obtain audit samples from the appropriate EPA Regional Office or from the responsible enforcement authority.

**Note:** The responsible enforcement agency should be notified at least 30 days prior to the test date to allow sufficient time for sample delivery.

7.2.4.2 Alternatively, audit cylinders obtained from a commercial gas manufacturer may be used provided: (a) the gas meets the conditions described

in Section 7.2.3, (b) the gas manufacturer certifies the audit cylinder as described in Section 7.2.3.1, and (c) the gas manufacturer obtains an independent analysis of the audit cylinders to verify this analysis. Independent analysis is defined here to mean analysis performed by an individual different than the individual who performs the gas manufacturer's analysis, while using calibration standards and analysis equipment different from those used for the gas manufacturer's analysis. Verification is complete and acceptable when the independent analysis concentration is within 5 percent of the gas manufacturer's concentration.

8.0 Sample Collection, Preservation, Storage, and Transport

**Note:** Performance of this method should not be attempted by persons unfamiliar with the operation of a gas chromatograph (GC) nor by those who are unfamiliar with source sampling, because knowledge beyond the scope of this presentation is required.

8.1 Bag Leak-Check. The following leak-check procedure is recommended, but not required, prior to sample collection. The post-test leak-check procedure is mandatory. Connect a water manometer and pressurize the bag to 5 to 10 cm H<sub>2</sub>O (2 to 4 in. H<sub>2</sub>O). Allow to stand for 10 min. Any displacement in the water manometer indicates a leak. Also, check the rigid container for leaks in this manner.

**Note:** An alternative leak-check method is to pressurize the bag to 5 to 10 cm H<sub>2</sub>O and allow it to stand overnight. A deflated bag indicates a leak. For each sample bag in its rigid container, place a rotameter in line between the bag and the pump inlet. Evacuate the bag. Failure of the rotameter to

register zero flow when the bag appears to be empty indicates a leak.

8.2 Sample Collection. Assemble the sample train as shown in Figure 106-1. Join the quick connects as illustrated, and determine that all connection between the bag and the probe are tight. Place the end of the probe at the centroid of the stack and start the pump with the needle valve adjusted to yield a flow that will fill over 50 percent of bag volume in the specific sample period. After allowing sufficient time to purge the line several times, change the vacuum line from the container to the bag and evacuate the bag until the rotameter indicates no flow. Then reposition the sample and vacuum lines and begin the actual sampling, keeping the rate proportional to the stack velocity. At all times, direct the gas exiting the rotameter away from sampling personnel. At the end of the sample period, shut off the pump, disconnect the sample line from the bag, and disconnect the vacuum line from the bag container. Protect the bag container from sunlight.

8.3 Sample Storage. Keep the sample bags out of direct sunlight. When at all possible, analysis is to be performed within 24 hours, but in no case in excess of 72 hours of sample collection. Aluminized Mylar bag samples must be analyzed within 24 hours.

8.4 Post-test Bag Leak-Check. Subsequent to recovery and analysis of the sample, leak-check the sample bag according to the procedure outlined in Section 8.1.

9.0 Quality Control

9.1 Miscellaneous Quality Control

Section	Quality control measure	Effect
10.3 .....	Chromatograph calibration .....	Ensure precision and accuracy of chromatograph.
11.1 .....	Audit sample analysis .....	Evaluate analytical technique and standards preparation.

9.2 Immediately after the preparation of the calibration curve and prior to the sample analyses, perform the analysis audit described in Appendix C, Procedure 2: "Procedure for Field Auditing GC Analysis."

10.0 Calibration and Standardization

**Note:** Maintain a laboratory log of all calibrations.

10.1 Preparation of Vinyl Chloride Standard Gas Mixtures. (Optional Procedure-delete if cylinder standards are used.) Evacuate a 16-inch square Tedlar bag that has passed a leak-check (described in Section 8.1) and meter in

5.0 liters of nitrogen. While the bag is filling, use the 0.5-ml syringe to inject 250 µl of 99.9+ percent vinyl chloride gas through the wall of the bag. Upon withdrawing the syringe, immediately cover the resulting hole with a piece of adhesive tape. The bag now contains a vinyl chloride concentration of 50 ppmv. In a like manner use the 50 µl syringe to prepare gas mixtures having 10-and 5-ppmv vinyl chloride concentrations. Place each bag on a smooth surface and alternately depress opposite sides of the bag 50 times to further mix the gases. These gas mixture standards may be used for 10 days from the date of preparation, after which time

new gas mixtures must be prepared. (Caution: Contamination may be a problem when a bag is reused if the new gas mixture standard is a lower concentration than the previous gas mixture standard.)

10.2 Determination of Vinyl Chloride Retention Time. (This section can be performed simultaneously with Section 10.3.) Establish chromatograph conditions identical with those in Section 11.3. Determine proper attenuator position. Flush the sampling loop with helium or nitrogen and activate the sample valve. Record the injection time, sample loop temperature, column temperature, carrier gas flow

rate, chart speed, and attenuator setting. Record peaks and detector responses that occur in the absence of vinyl chloride. Maintain conditions with the equipment plumbing arranged identically to Section 11.2, and flush the sample loop for 30 seconds at the rate of 100 ml/min with one of the vinyl chloride calibration mixtures. Then activate the sample valve. Record the injection time. Select the peak that corresponds to vinyl chloride. Measure the distance on the chart from the injection time to the time at which the peak maximum occurs. This quantity divided by the chart speed is defined as the retention time. Since other organics may be present in the sample, positive identification of the vinyl chloride peak must be made.

**10.3 Preparation of Chromatograph Calibration Curve.** Make a GC measurement of each gas mixture standard (described in Section 7.2.3 or 10.1) using conditions identical to those listed in Sections 11.2 and 11.3. Flush the sampling loop for 30 seconds at the rate of 100 ml/min with one of the standard mixtures, and activate the sample valve. Record the concentration of vinyl chloride injected ( $C_c$ ), attenuator setting, chart speed, peak area, sample loop temperature, column temperature, carrier gas flow rate, and retention time. Record the barometric pressure. Calculate  $A_c$ , the peak area multiplied by the attenuator setting. Repeat until two consecutive injection areas are within 5 percent, then plot the average of those two values versus  $C_c$ . When the other standard gas mixtures have been similarly analyzed and plotted, draw a straight line through the points derived by the least squares method. Perform calibration daily, or before and after the analysis of each emission test set of bag samples, whichever is more frequent. For each group of sample analyses, use the average of the two calibration curves which bracket that group to determine the respective sample concentrations. If the two calibration curves differ by more than 5 percent from their mean value, then report the final results by both calibration curves.

**12.3 Vinyl Chloride Concentration.** From the calibration curves prepared in Section 10.3, determine the average

### 11.0 Analytical Procedure

**11.1 Audit Sample Analysis.** Immediately after the preparation of the calibration curve and prior to the sample analyses, perform the analysis audit described in Procedure 2 of appendix C to this part: "Procedure for Field Auditing GC Analysis."

**11.2 Sample Recovery.** With a new piece of Teflon tubing identified for that bag, connect a bag inlet valve to the gas chromatograph sample valve. Switch the valve to receive gas from the bag through the sample loop. Arrange the equipment so the sample gas passes from the sample valve to 100-ml/min rotameter with flow control valve followed by a charcoal tube and a 1-in. H<sub>2</sub>O pressure gauge. Maintain the sample flow either by a vacuum pump or container pressurization if the collection bag remains in the rigid container. After sample loop purging is ceased, allow the pressure gauge to return to zero before activating the gas sampling valve.

#### 11.3 Analysis.

**11.3.1** Set the column temperature to 100 °C (210 °F) and the detector temperature to 150 °C (300 °F). When optimum hydrogen and oxygen (or air) flow rates have been determined, verify and maintain these flow rates during all chromatography operations. Using helium or nitrogen as the carrier gas, establish a flow rate in the range consistent with the manufacturer's requirements for satisfactory detector operation. A flow rate of approximately 40 ml/min should produce adequate separations. Observe the base line periodically and determine that the noise level has stabilized and that base line drift has ceased. Purge the sample loop for 30 seconds at the rate of 100 ml/min, shut off flow, allow the sample loop pressure to reach atmospheric pressure as indicated by the H<sub>2</sub>O manometer, then activate the sample valve. Record the injection time (the position of the pen on the chart at the time of sample injection), sample number, sample loop temperature, column temperature, carrier gas flow rate, chart speed, and attenuator setting. Record the barometric pressure. From the chart, note the peak having the

retention time corresponding to vinyl chloride as determined in Section 10.2. Measure the vinyl chloride peak area,  $A_m$ , by use of a disc integrator, electronic integrator, or a planimeter. Measure and record the peak heights,  $H_m$ . Record  $A_m$  and retention time. Repeat the injection at least two times or until two consecutive values for the total area of the vinyl chloride peak agree within 5 percent of their average. Use the average value for these two total areas to compute the bag concentration.

**11.3.2** Compare the ratio of  $H_m$  to  $A_m$  for the vinyl chloride sample with the same ratio for the standard peak that is closest in height. If these ratios differ by more than 10 percent, the vinyl chloride peak may not be pure (possibly acetaldehyde is present) and the secondary column should be employed (see Section 6.3.2.2).

**11.4 Determination of Bag Water Vapor Content.** Measure the ambient temperature and barometric pressure near the bag. From a water saturation vapor pressure table, determine and record the water vapor content of the bag,  $B_{wb}$ , as a decimal figure. (Assume the relative humidity to be 100 percent unless a lesser value is known.)

### 12.0 Calculations and Data Analysis

#### 12.1 Nomenclature.

$A_m$  = Measured peak area.

$A_f$  = Attenuation factor.

$B_{wb}$  = Water vapor content of the bag sample, as analyzed, volume fraction.

$C_b$  = Concentration of vinyl chloride in the bag, ppmv.

$C_c$  = Concentration of vinyl chloride in the standard sample, ppmv.

$P_i$  = Laboratory pressure at time of analysis, mm Hg.

$P_r$  = Reference pressure, the laboratory pressure recorded during calibration, mm Hg.

$T_i$  = Absolute sample loop temperature at the time of analysis, °K (°R).

$T_r$  = Reference temperature, the sample loop temperature recorded during calibration, °K (°R).

**12.2 Sample Peak Area.** Determine the sample peak area,  $A_c$ , as follows:

$$A_c = A_m A_f \quad \text{Eq. 106-1}$$

concentration value of vinyl chloride,  $C_c$ , that corresponds to  $A_c$ , the sample

peak area. Calculate the concentration of vinyl chloride in the bag,  $C_b$ , as follows:

$$C_b = \frac{C_c P_r T_i}{P_i T_r (1 - B_{wb})} \quad \text{Eq. 106-2}$$

### 13.0 Method Performance

13.1 Analytical Range. This method is designed for the 0.1 to 50 parts per million by volume (ppmv) range. However, common gas chromatograph (GC) instruments are capable of detecting 0.02 ppmv vinyl chloride. With proper calibration, the upper limit may be extended as needed.

### 14.0 Pollution Prevention, [Reserved]

### 15.0 Waste Management, [Reserved]

### 16.0 References

1. Brown D.W., E.W. Loy, and M.H. Stephenson. Vinyl Chloride Monitoring Near

the B. F. Goodrich Chemical Company in Louisville, KY. Region IV, U.S. Environmental Protection Agency, Surveillance and Analysis Division, Athens, GA. June 24, 1974.

2. G.D. Clayton and Associates. Evaluation of a Collection and Analytical Procedure for Vinyl Chloride in Air. U.S. Environmental Protection Agency, Research Triangle Park, N.C. EPA Contract No. 68-02-1408, Task Order No. 2, EPA Report No. 75-VCL-1. December 13, 1974.

3. Midwest Research Institute. Standardization of Stationary Source Emission Method for Vinyl Chloride. U.S. Environmental Protection Agency, Research Triangle Park, N.C. Publication No. EPA-600/4-77-026. May 1977.

4. Scheil, G. and M.C. Sharp. Collaborative Testing of EPA Method 106 (Vinyl Chloride) that Will Provide for a Standardized Stationary Source Emission Measurement Method. U.S. Environmental Protection Agency, Research Triangle Park, N.C. Publication No. EPA 600/4-78-058. October 1978.

### 17.0 Tables, Diagrams Flowcharts, and Validation Data.

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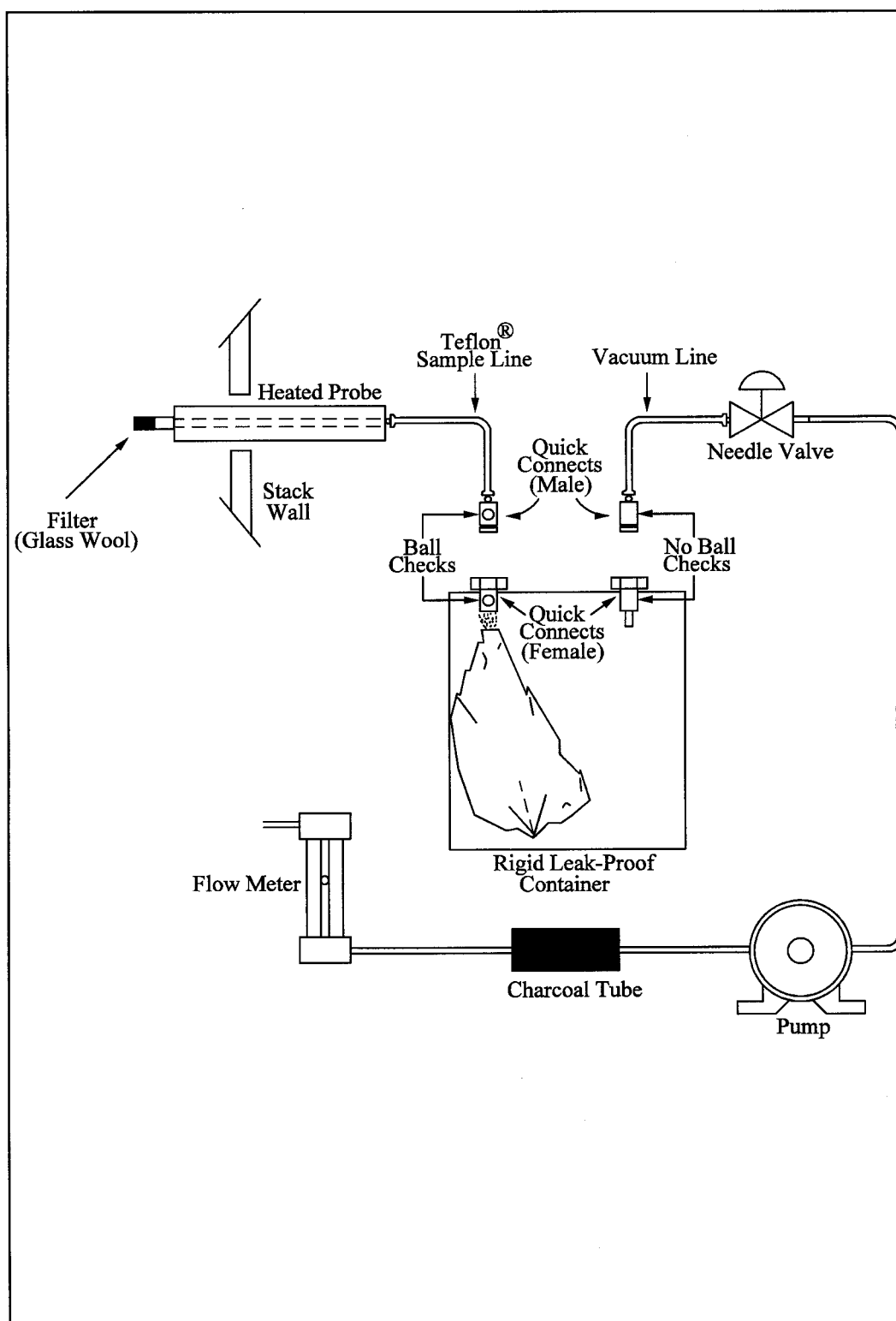


Figure 106-1. Integrated-bag sampling train.

**Method 107—Determination of Vinyl Chloride Content of In-Process Wastewater Samples, and Vinyl Chloride Content of Polyvinyl Chloride Resin Slurry, Wet Cake, and Latex Samples**

**Note:** Performance of this method should not be attempted by persons unfamiliar with

the operation of a gas chromatograph (GC) nor by those who are unfamiliar with source sampling, because knowledge beyond the scope of this presentation is required. This method does not include all of the specifications (e.g., equipment and supplies) and procedures (e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from

other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 106.

### 1.0 Scope and Application

#### 1.1 Analytes.

Analyte	CAS No.	Sensitivity
Vinyl Chloride (CH <sub>2</sub> :CHCl) .....	75-01-4	Dependent upon analytical equipment.

1.2 Applicability. This method is applicable for the determination of the vinyl chloride monomer (VCM) content of in-process wastewater samples, and the residual vinyl chloride monomer (RCVM) content of polyvinyl chloride (PVC) resins, wet, cake, slurry, and latex samples. It cannot be used for polymer in fused forms, such as sheet or cubes. This method is not acceptable where methods from section 304(h) of the Clean Water Act, 33 U.S.C. 1251 *et seq.* (the Federal Water Pollution Control Amendments of 1972 as amended by the Clean Water Act of 1977) are required.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

### 2.0 Summary of Method

2.1 The basis for this method relates to the vapor equilibrium that is established at a constant known temperature in a closed system between RVC, PVC resin, water, and air. The RVC in a PVC resin will equilibrate rapidly in a closed vessel, provided that the temperature of the PVC resin is maintained above the glass transition temperature of that specific resin.

2.2 A sample of PVC or in-process wastewater is collected in a vial or bottle and is conditioned. The headspace in the vial or bottle is then analyzed for vinyl chloride using gas chromatography with a flame ionization detector.

### 3.0 Definitions [Reserved]

### 4.0 Interferences

4.1 The chromatograph columns and the corresponding operating parameters herein described normally provide an adequate resolution of vinyl chloride; however, resolution interferences may be encountered on some sources. Therefore, the chromatograph operator shall select the column and operating parameters best suited to his particular analysis requirements, subject to the approval of the Administrator. Approval is automatic provided that confirming

data are produced through an adequate supplemental analytical technique, such as analysis with a different column or GC/mass spectroscopy, and that these data are made available for review by the Administrator.

### 5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Toxic Analyte. Care must be exercised to prevent exposure of sampling personnel to vinyl chloride, which is a carcinogen. Do not release vinyl chloride to the laboratory atmosphere during preparation of standards. Venting or purging with VCM/air mixtures must be held to a minimum. When they are required, the vapor must be routed to outside air. Vinyl chloride, even at low ppm levels, must never be vented inside the laboratory. After vials have been analyzed, the gas must be vented prior to removal of the vial from the instrument turntable. Vials must be vented through a hypodermic needle connected to an activated charcoal tube to prevent release of vinyl chloride into the laboratory atmosphere. The charcoal must be replaced prior to vinyl chloride breakthrough.

### 6.0 Equipment and Supplies

6.1 Sample Collection. The following equipment is required:

6.1.1 Glass bottles. 60-ml (2-oz) capacity, with wax-lined screw-on tops, for PVC samples.

6.1.2 Glass Vials. Headspace vials, with Teflon-faced butyl rubber sealing discs, for water samples.

6.1.3 Adhesive Tape. To prevent loosening of bottle tops.

6.2 Sample Recovery. The following equipment is required:

6.2.1 Glass Vials. Headspace vials, with butyl rubber septa and aluminum caps. Silicone rubber is not acceptable.

6.2.2 Analytical Balance. Capable of determining sample weight within an accuracy of  $\pm 1$  percent.

6.2.3 Vial Sealer. To seal headspace vials.

6.2.4 Syringe. 100-ml capacity.

6.3 Analysis. The following equipment is required:

6.3.1 Headspace Sampler and Chromatograph. Capable of sampling and analyzing a constant amount of headspace gas from a sealed vial, while maintaining that vial at a temperature of  $90^\circ\text{C} \pm 0.5^\circ\text{C}$  ( $194^\circ\text{F} \pm 0.9^\circ\text{F}$ ). The chromatograph shall be equipped with a flame ionization detector (FID). Perkin-Elmer Corporation Models F-40, F-42, F-45, HS-6, and HS-100, and Hewlett-Packard Corporation Model 19395A have been found satisfactory. Chromatograph backflush capability may be required.

6.3.2 Chromatographic Columns. Stainless steel 1 m by 3.2 mm and 2 m by 3.2 mm, both containing 50/80-mesh Porapak Q. Other columns may be used provided that the precision and accuracy of the analysis of vinyl chloride standards are not impaired and information confirming that there is adequate resolution of the vinyl chloride peak are available for review. (Adequate resolution is defined as an area overlap of not more than 10 percent of the vinyl chloride peak by an interferant peak. Calculation of area overlap is explained in Procedure 1 of appendix C to this part: "Determination of Adequate Chromatographic Peak Resolution.") Two 1.83 m columns, each containing 1 percent Carbowax 1500 on Carbowax B, have been found satisfactory for samples containing acetaldehyde.

6.3.3 Temperature Sensor. Range 0 to  $100^\circ\text{C}$  ( $32$  to  $212^\circ\text{F}$ ) accurate to  $0.1^\circ\text{C}$ .

6.3.4 Integrator-Recorder. To record chromatograms.

6.3.5 Barometer. Accurate to 1 mm Hg.